NATIONAL URANIUM TAILINGS PROGRAM

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STUDY OF THE GEOCHEMISTRY OF THORIUM IN URANIUM MILL TAILINGS

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by

MELIS CONSULTING ENGINEERS LTD.
in association with
SASKATCHEWAN RESEARCH COUNCIL
and
SENES CONSULTANTS LIMITED

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MELIS CONSULTING ENGINEERS LTD.

Metallurgical Engineering Services
519 45th Street West
Saskatoon, Saskatchewan, Canada
S7L 5Z9
(306) 652-4084
Telex: 074-2683 (NORPLEX)

October 10, 1986

Department of Energy, Mines and Resources
CANMET
National Uranium Tailings Program
555 Booth Street
Ottawa, Ontario
K1A 0G1

Project No.: MCEL 114

Attention: Dr. C. Smith

DSS Contract No.: 23317-6-1723/01-SQ

Dear Dr. Smith:

We are pleased to submit twenty-five copies of the Final Report entitled "Study of the Geochemistry of Thorium in Uranium Mill Tailings". This work has been completed for the National Uranium Tailings Program by Melis Consulting Engineers Ltd. in association with the Saskatchewan Research Council and SENES Consultants Limited.

We trust the results of the study prove useful to the National Uranium Tailings Program and we appreciate the opportunity of being of service to the Department of Energy, Mines and Resources on this project. We remain available to discuss any aspect of the report at your convenience.

Respectfully submitted,

MELIS CONSULTING ENGINEERS LTD.

L.A. Melis, P.Eng.
Principal

LAM/bh

Enclosures

STUDY OF THE GEOCHEMISTRY OF THORIUM IN URANIUM MILL TAILINGS

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The assistance and cooperation of Rio Algom Limited's Process Development Department in securing the Quirke mill uranium tailings sample was greatly appreciated and is hereby acknowledged.

STUDY OF THE GEOCHEMISTRY OF THORIUM IN URANIUM MILL TAILINGS

1.0 SUMMARY

The National Uranium Tailings Program office of the Department of Energy, Mines and Resources commissioned Melis Consulting Engineers Ltd. to perform a study on the geochemistry of thorium in uranium mill tailings. This work was carried out in association with the Saskatchewan Research Council and SENES Consultants Limited.

The tailings used for the investigation was neutralized tailings obtained from the Quirke mill tailings neutralization circuit in Elliot Lake, Ontario. Laboratory tests were completed to provide experimental data for geochemical modelling. The tailings solids were submitted to batch and column leaching experiments using varying ferrous sulphate concentrations at different pH levels. The leachates generated in the batch leach tests were submitted to oxidation and precipitation tests for investigating the co-precipitation behaviour of thorium in sulphate media.

Water wash tests indicated insignificant water dissolution of thorium or thorium-230 from the tailings solids. On the other hand the dissolution of thorium, thorium-230 and thorium-232 was in the range of 50 to 60% with pH 2, 13.5 g/L $FeSO_4$ leach solution. Extractions decreased with increasing pH levels with only 1 to 2% extractions being obtained at pH 5.

Varying ferrous sulphate concentrations at pH 3.5 resulted in thorium extractions of approximately 25% at 21.8 g/L $FeSO_4$ down to only 1 to 2% at 1.35 g/L $FeSO_4$ concentration.

The lysimeter tests generally confirmed the batch leach results although reaction kinetics were, as expected, much slower. Decreasing the specific flowrate to the column generally increased extractions due to increased leachate contact time with the tailings solids.

Oxidation and neutralization of the leachate (to pH 4) resulted in virtually complete precipitation of iron and thorium and its isotopes.

From a geochemical modelling standpoint thorium hydroxide appears to control the dissolution of thorium. As predicted from equilibrium modelling, sulphate complexing, ionic strength, and pH are the prime factors controlling solubility. Thorium precipitates as a mixture of amorphous and crystalline thorium hydroxide, making geochemical predictions of solubility very difficult. At low pH, equilibrium is generally not obtained as the thorium hydroxide dissolution rate is quite low.

Ferrous ion oxidation and precipitation play a major role in the removal of thorium from solution by adsorption. Distribution coefficients (K_D) measured were of the order 20,000 mL/g for ferric hydroxide precipitation.

Mineralogically, it is apparent that a portion of the thorium-232 and thorium-230 are present in different mineral precipitates. This results in approximately 65 percent of thorium-232 being leachable while approximately 80 percent of the thorium-230 is believed to be leachable.

STUDY OF THE GEOCHEMISTRY OF THORIUM IN URANIUM MILL TAILINGS

2.0 INTRODUCTION

The National Uranium Tailings Program (NUTP) was established by the Department of Energy, Mines and Resources to address the long-term environmental concern of mill tailings from uranium mining operations. Its main goal is to provide a scientifically credible information base on which decisions can be made, with a known degree of confidence, in establishing reasonable criteria for the protection of the environment, and which can also be used to propose practical guidelines for uranium tailings management.

While radium-226 is the major radioactive component in uranium mill tailings, the possible contribution of thorium-230 to radioactive contamination, especially in Elliot Lake tailings, cannot be ignored. Because of its long half-life, and as a long-term regenerant of radium-226, possible movement of thorium-230 from the tailings to the environment constitutes a potential long-term concern. A better understanding of the geochemistry of thorium-230 is therefore required in order to assist in the prediction of the long-term behaviour of thorium-230 in uranium mill tailings.

A study was commissioned by the NUTP office to investigate the behaviour of thorium-230 in uranium mill tailings from the Elliot Lake area of northern Ontario. The study included an experimental evaluation of the release of thorium and thorium-230 from tailings as a function of pH and ferrous iron concentration and an investigation of the co-precipitation of thorium-230 in the leachate sulphate medium as a function of pH and ferric iron concentration. The experimental data were used to arrive at an appropriate geochemical equilibrium model to predict the future behaviour of thorium-230 in uranium mill tailings.

Melis Consulting Engineers Ltd. (MCEL) completed this work for the Department of Energy, Mines and Resources under contract to the Department of Supply and

Services. The testwork component of the study was carried out at the Saskatchewan Research Council (SRC) facilities in Saskatchewan under the direction of MCEL. SENES Consultants Limited were retained to derive a geochemical equilibrium model of thorium in uranium mill tailings utilizing the experimental data generated in the laboratory tests.

3.0 LABORATORY TESTWORK

3.1 GENERAL

To obtain the appropriate experimental data for geochemical modelling, the laboratory testwork was performed in different stages. An appropriate sample of "fresh" neutralized uranium mill tailings was first obtained from the Quirke uranium mine in Elliot Lake, Ontario. The physical and chemical characteristics of the tailings solids as received were first determined along with the chemical make-up of the tailings porewater in terms of the elements of interest to the study.

Water wash tests, pH variability batch leach tests and ferrous sulphate variability batch leach tests were then completed to determine the leaching characteristics of thorium and thorium-230 in neutralized uranium mill tailings. The leachates from the pH and ferrous sulphate variability tests were then submitted to oxidation tests to assess the co-precipitation of thorium and thorium-230 in oxidized sulphate medium.

Leaching of the uranium mill tailings was then evaluated in column lysimeters with different pH and ferrous sulphate concentrations. The minimum and maximum leaching extraction conditions were established in the batch leach variability tests. Different flowrates were used in the lysimeter tests to determine the effect of percolation rates on thorium and thorium-230 chemical mobility. The maximum flowrate used in these lysimeter tests was restricted by the permeability of the tailings solids.

The experimental data generated from the above tests were then interpreted and analysed in geochemical modelling studies to predict the long-term behaviour of thorium in uranium mill tailings.

3.2 SAMPLE DESCRIPTION

The uranium mill tailings sample used in the laboratory testwork was obtained from the Quirke Mine operation of Rio Algom Limited in Elliot Lake, Ontario.

The Quirke milling circuit is typical of the Elliot Lake area uranium operations. Ground ore is leached with sulfuric acid in air-agitated pachucas at elevated temperatures (80|C) and ambient pressures. The uranium-rich solution in the leach pulp is separated from the leach residue by wash cyclones and counter-current decantation (CCD) in six stages of thickeners. Yellowcake is produced by precipitation of ion exchange eluate with ammonia. Uranium recovery from minewater is achieved by precipitation of acidic minewater with lime and re-dissolution of the uranium-containing precipitate.

Tailings slurry, consisting of CCD tails (slimes) and washed cyclone underflow (coarse), is neutralized with limestone to pH 3.5 and lime to pH 10-11 in a series of five tailings neutralization pachucas. The neutralized tailings slurry is pumped to the Bud Lake tailings basin where tailings decant water and acidic seepage water is treated with lime and barium chloride. The treated water is clarified in a series of three unlined settling ponds prior to discharge to the Serpent River system.

The tailings sample used in the testwork was taken directly from the last tailings neutralization pachuca in the Quirke mill circuit on April 21, 1986. The bulk sample was received at SRC's facilities on May 5, 1986. The tailings solids, weighing approximately 200 kg (dry basis) with a moisture content of 12.8% H_2O, were received in a plastic-lined 200 L drum. Tailings porewater, representing tailings water present in the slurry at the time of sampling, was received separately in a 20 L plastic container.

The tailings solids were mixed and transferred to a clean covered 200 L plastic container purged with argon gas to prevent oxidation of the tailings material.

The tailings porewater was re-equilibrated with tailings solid by contacting two separate 500 g tailings grab samples with 2.5 L of porewater in a beaker,

manually mixing the slurry, and allowing it to stand for 30 minutes. The slurry was then filtered and the porewater and tailings solids samples were analysed in duplicate. The analytical results are given in Table 3-1. The liquid analysis, as for all liquid analysis given in this report, is for liquids filtered through a 3 micron millipore filter.

The total thorium content of the tailings solids sample received for test purposes was 0.015% Th. This analytical head compares favourably to the average head of 0.0175% Th as calculated from product analyses of the batch leach tests. The thorium content of the tailings sample used in the testwork is approximately half of the expected thorium concentration for Elliot Lake ores (0.03% to 0.04% Th). This could have been due to a low ratio of monazite to brannerite or simply due to lower grade feed in the mill circuit at the time of sampling.

The calcium and sulphate assays of the porewater reflect the limited solubility of gypsum. The iron concentration of the porewater (<0.01 mg/L) is indicative of the high pH of the porewater resulting from lime neutralization of the acid tailings in the tailings neutralization circuit.

The particle size analysis of the tailings as-received is listed in Table 3-2. The screen analysis of 13.9% minus 74 microns (200 mesh) is significantly coarser than anticipated values since the average particle size of Elliot Lake tailings is typically 50-55% minus 74 microns.

The coarseness of the tailings sample received for test purposes was likely due to imbalances in the Quirke mill circuit at the time of sampling. As briefly described above the acid leach pulp in the Quirke mill is partially neutralized (pH 1.9) then processed through a cyclone wash circuit to recover a slimes pulp containing the dissolved uranium. This slimes pulp is thickened and washed in a CCD circuit to recover pregnant solution and produce low uranium tailings solids. The tailings from the CCD circuit are mixed with the coarser cyclone tails from the cyclone wash circuit in the tailings neutralization circuit. The combined neutralized tailings are then discharged to the tailings area.

TABLE 3-1

URANIUM MILL TAILINGS AND POREWATER ANALYSES

Analyte	Tailings Solids (%)			Tailings Porewater (mg/L)(1)	
	A	B	C(3)	A	B
Ca	0.25	0.24		650	650
SO_4	9.20(2)	9.10(2)		1,720	1,700
Fe	2.70	2.70		< 0.01	< 0.01
Th	0.0153	0.0152	0.0175	0.0075	0.013
		Bq/g		Bq/L	
Th-228	0.60	0.55	0.8	0.03	0.05
Th-230	2.5	2.5	2.45	0.20	0.40
Th-232	0.60	0.55	0.8	0.03	0.05
pH				9.63	9.74

NOTES: (1) filtered through 3 micron millipore filter

(2) sulphate assay based on total sulphur content

(3) average calculated head as determined from product analyses of the batch leach tests

TABLE 3-2

TAILINGS SOLIDS SCREEN ANALYSIS

Fraction			
Microns	Mesh	Weight %	Cumulative Weight %
+420	+35	14.8	14.8
-420+300	-35+48	15.0	29.8
-300+212	-48+65	23.0	52.8
-212+149	-65+100	15.2	68.0
-149+74	-100+200	18.1	86.1
-74+43	-200+325	10.7	96.8
-43	-325	3.2	100.0

Hence circuit conditions that existed at the time of sampling were probably low flow from the CCD circuit, in order to increase the CCD tailings density and hence improve CCD wash efficiencies, and normal or high flows of coarse cyclone underflow pulp. This would result in a coarse tailings product being pumped to the tailings area until CCD and cyclone flows stabilized in the mill circuit. The implications to the study would be the presence of a higher fraction of unreacted monazite in the tailings solids sample used for the testwork.

Laboratory tests were well underway by the time particle size and head assays were received and schedule restrictions would not have allowed sufficient time to secure another tailings sample from the Quirke mill. Evaluation of preliminary results at the onset of the program indicated that the experimental data obtained from the tailings sample used in the test program would provide modelling results which would be representative of the Elliot Lake tailings. Hence the testwork was completed on the Quirke mill tailings sample as received.

3.3 WATER WASH TESTS

3.3.1 Methodology

Two separate test portions of tailings were washed with deionized water to assess the water solubility of thorium and thorium-230 in the tailings solids.

A 500 g (dry basis) sample of tailings was mechanically agitated with 2.5 L of deionized water for 30 minutes after which 2 L of liquid was removed by filtration. A second-stage water wash was effected by adding an additional 2 L of water and stirring for 45 minutes. The second-stage filtrate was collected (2 L) and replaced with 2 L of water to provide a third-stage wash for 30 minutes. The final third-stage filtrate was collected by filtering the complete pulp. All three filtrates and the water-washed solids were then submitted for thorium analysis.

3.3.2 Results

The filtrate and solids analyses for the duplicate water wash tests are summarized in Table 3-3. The assays indicate that roughly equal fractions of thorium and thorium-230 were solubilized into the deionized water in each of the three water wash stages. The concentrations are so low however that the effective water solubilization of thorium is insignificant relative to the total amount of thorium present in the tailings solids.

3.3.3 Tessier Extraction

The water-washed solids were also analyzed for iron, thorium and thorium-230 present as the hydrous oxide/hydroxide by the Tessier extraction method (Tessier, 1979). The Tessier extraction method is based on the extraction of thorium hydrous oxide/hydroxide by contacting a 5 g sample, in this case tailings solids, with 100 mL of 0.04 M hydroxylamine hydrochloride in 25% (v/v) acetic acid for 6 hours at a temperature just below the boiling point with mild stirring of the slurry. After the leach is complete the liquid is recovered by centrifuging and analysed for thorium and its isotopes in the normal manner. This method thus provides an analysis of thorium and its isotopes present in the solids as hydrous oxide/hydroxide.

TABLE 3-3

WATER WASH TEST RESULTS

TEST A

Analyte		Filtrates			Solids
		Wash No. 1	Wash No. 2	Wash No. 3	
Th	(mg/L)	0.019	0.030	0.035	0.0160%
Th-228	(Bq/L)	0.08	0.13	0.15	0.55 Bq/g
Th-230	(Bq/L)	0.50	0.80	0.80	3.5 Bq/g
Th-232	(Bq/L)	0.08	0.13	0.15	0.55 Bq/g

TEST B

Th	(mg/L)	0.025	0.025	0.019	0.0205%
Th-228	(Bq/L)	0.11	0.11	0.08	0.70 Bq/g
Th-230	(Bq/L)	0.70	0.70	0.45	3.0 Bq/g
Th-232	(Bq/L)	0.11	0.11	0.08	0.70 Bq/g

The results of the Tessier analysis are given in Table 3-4. A comparison of these thorium analyses with those reported for the water wash tests in Table 3-3 indicates that the Tessier extraction removes approximately 60-65% of the thorium present in the tailings and about 45% of the thorium-230 isotope. This analysis then infers that the thorium removed by the Tessier extraction method is present as a hydrous oxide/hydroxide.

It can therefore be interpreted that approximately 60-65% of the thorium originally present in the ore as thorium-bearing minerals is dissolved in the acid leach circuit and re-precipitated as hydrous oxide/hydroxides in the tailings neutralization circuit. This value is in agreement with actual plant circuit data for thorium dissolution in a uranium acid leach circuit. The 45% value for thorium-230 can be considered as an anomalous value since this isotope would be expected to behave in a similar matter as elemental thorium in the uranium leaching circuit. Subsequent results generally showed the same mobilization characteristics for thorium and thorium-230 as indicated by the Tessier extraction (see Sections 3.4, 3.5 and 3.7).

TABLE 3-4

WATER WASH TEST SOLIDS
ANALYSIS OF RESIDUE AFTER TESSIER EXTRACTION

Analyte	Test A	Test B
Fe (%)	0.204	0.242
Th (%)	0.006	0.007
Th-228 (Bq/g)	0.25	0.30
Th-230 (Bq/g)	1.8	1.8
Th-232 (Bq/g)	0.25	0.30

3.4 pH VARIABILITY TESTS

3.4.1 Methodology

The potential re-dissolution of thorium, thorium-230 and thorium-232 in acidic sulphate media was investigated by submitting batch samples of tailings solids to leaching tests using ferrous sulphate solution as lixiviant.

Test portions (1.1 kg) of tailings were batch leached with 4.4 L of 13.5 g/L $FeSO_4$ solution at four different pH values, namely pH 2,3,4, and 5. The ferrous sulphate solution was made up as required using chemical grade $FeSO_4.7H_2O$ reagent.

The leach tests were carried out at 20% solids in 20 L plastic pails fitted with lids. An inert leach atmosphere was provided over the leach pulp by sparging argon gas from a manifold system through a small hole in the pail lids. Proper slurry agitation to the four leach pails was provided by a common-drive mechanical mixer to afford the same mixing intensity in all four leach tests. Thorough agitation of the leach slurry was insured by fitting stainless steel baffles in the plastic pails.

The desired pH values of 2,3,4 and 5 were reached by the addition of 50 g/L H_2SO_4 solution. The initial pH of the leach solution when mixed with the tailings was approximately 5.8. The pH of each test was monitored regularly during the leaching period with pH adjustments being made by periodic addition of sulfuric acid and, on occasion, lime to maintain a constant pH.

In the first set of leach tests the leach slurry was sampled at regular intervals and the leachate analysed for thorium-230 to determine the reaction time required to either attain equilibrium or achieve maximum thorium-230 leaching for the four pH values. Once the optimum reaction time was determined then a larger sample of tailings (2.2 kg) was used to provide sufficient leachate for analysis and for subsequent leachate oxidation tests.

In the first experimental leaching run (with periodic withdrawal of slurry samples) the sampling times used were 4,8,17 and 48 hours. The thorium-230

analyses from this first run were erratic hence it was decided to consider this first test as a preliminary run-in test.

The leach test was then repeated with sampling times of 4,24,48 and 72 hours. The 1 L slurry samples taken at increasing reaction times were withdrawn from the agitated pulp by means of a peristaltic pump. The slurry sample was flocculated with 10 mL of 1 g/L Percol 351 flocculant solution prior to filtering to recover the leachate sample. The leachate sample was then filtered through a 3 micron millipore filter, preserved with 10 mL of nitric acid, and submitted for thorium-230 analysis.

Using the optimum leaching time determined for each pH value (see Section 3.4.2) the four leach tests were repeated at pH 2,3,4 and 5 using 2.2 kg of tailings solids and 8.8 L of 13.5 g/L $FeSO_4$ solution. The leach for each pH value was carried out exactly as described above but slurry samples were not withdrawn during the leach other than for pH measurements. A 48-hour retention time was used for the pH 2 and pH 3 leach tests and a 30-hour retention time was used for the pH 4 and pH 5 leach tests. It was noticed that the pH in the two high pH tests tended to drift downwards due to a minor amount of oxidation taking place thereby requiring lime addition to maintain a constant pH. The low pH tests, pH 2 and pH 3, tended to drift upwards in pH therefore requiring periodic acid addition to maintain a constant pH. The higher acid concentrations present in the pH 2 and pH 3 tests would have resulted in a minor amount of acid being consumed by the ore minerals still present in the tailings solids.

At the end of the leach period 30 mL of flocculant solution was added to the total slurry to assist in filtration of the pulp. A portion of the filtrate, 1 L, was submitted for analysis and the remaining filtrate was retained for the leachate oxidation tests. The solids were washed with water prior to submitting for analysis.

3.4.2 Results

The test results for increasing leach retention time at the four different pH values are listed in Table 3-5. The thorium-230 assays, the isotope of

TABLE 3-5

pH VARIABILITY TESTS (13.5 g/L $FeSO_4$)
LEACHATE THORIUM ANALYSIS AT DIFFERENT REACTION TIMES (Bq/L)

Analyte	Leach Time (h)	pH 2	pH 3	pH 4	pH 5
Th-228	4	30	45	4.5	1.4
	24	85	40	16	5.5
	48	85	35	8.5	4.5
	72	70	45	4.0	1.4
Th-230	4	170	290*	25	7.0
	24	480	230	80	30
	48	490	200	50	25
	72	400	250	25	8.0
Th-232	4	30	45	4.5	1.4
	24	85	40	16	5.5
	48	85	35	8.5	4.5
	72	70	45	4.0	1.4

* likely an anomalous result when compared to the analysis trend for pH 2, 4 and 5

interest, are depicted graphically in Figure 3-1 for the pH 2 and pH 3 tests and in Figure 3-2 for the pH 4 and pH 5 tests.

The results indicate that there is a constant trend in increasing Th-230 concentration in the leachate to a certain maximum followed by a decrease in thorium-230 content with increasing leach retention time. The leach times resulting in maximum extraction of thorium-230 were selected from these graphs for each pH value. Consequently a 30-hour leach time was selected for the pH 4 and pH 5 leach tests and a 48-hour leach time was used for the pH 2 and pH 3 leach tests.

The results of the fixed leach time tests on 2.2 kg of tailings solids at pH 2,3,4 and 5 are summarized in Table 3-6 along with the calculated head analysis for each test. As can be seen from these results calcium, sulphate and iron levels in the leachates remain relatively constant for the four pH values but the total thorium and thorium isotope analyses decrease significantly with increasing pH values.

Material balance calculations for each test, based on the product analyses given in Table 3-6, provide the effective extraction of thorium from tailings solids by ferrous sulphate solution under increasing acidic conditions (pH 5 to pH 2). The calculated percent extraction values for pH 2,3,4 and 5 are given in Table 3-7 and depicted in Figure 3-3.

Comparing the calculated extraction values to the Tessier Extraction results given in Section 3.3.3 above it can be interpreted that the hydrous oxide/hydroxide forms of thorium, thorium-230 and thorium-232 in the tailings solids are leached almost completely at pH 2 with 13.5 g/L $FeSO_4$ solution but are virtually untouched at pH 5. Consequently any natural decrease in porewater pH in uranium tailings ponds to low pH levels would lead to the re-solubilization of thorium, thorium-230 and thorium-232 hydrous oxide/hydroxides present in the tailings solids.

FIGURE 3-1
pH VARIABILITY TESTS
LEACHATE Th-230 ANALYSIS VS TIME

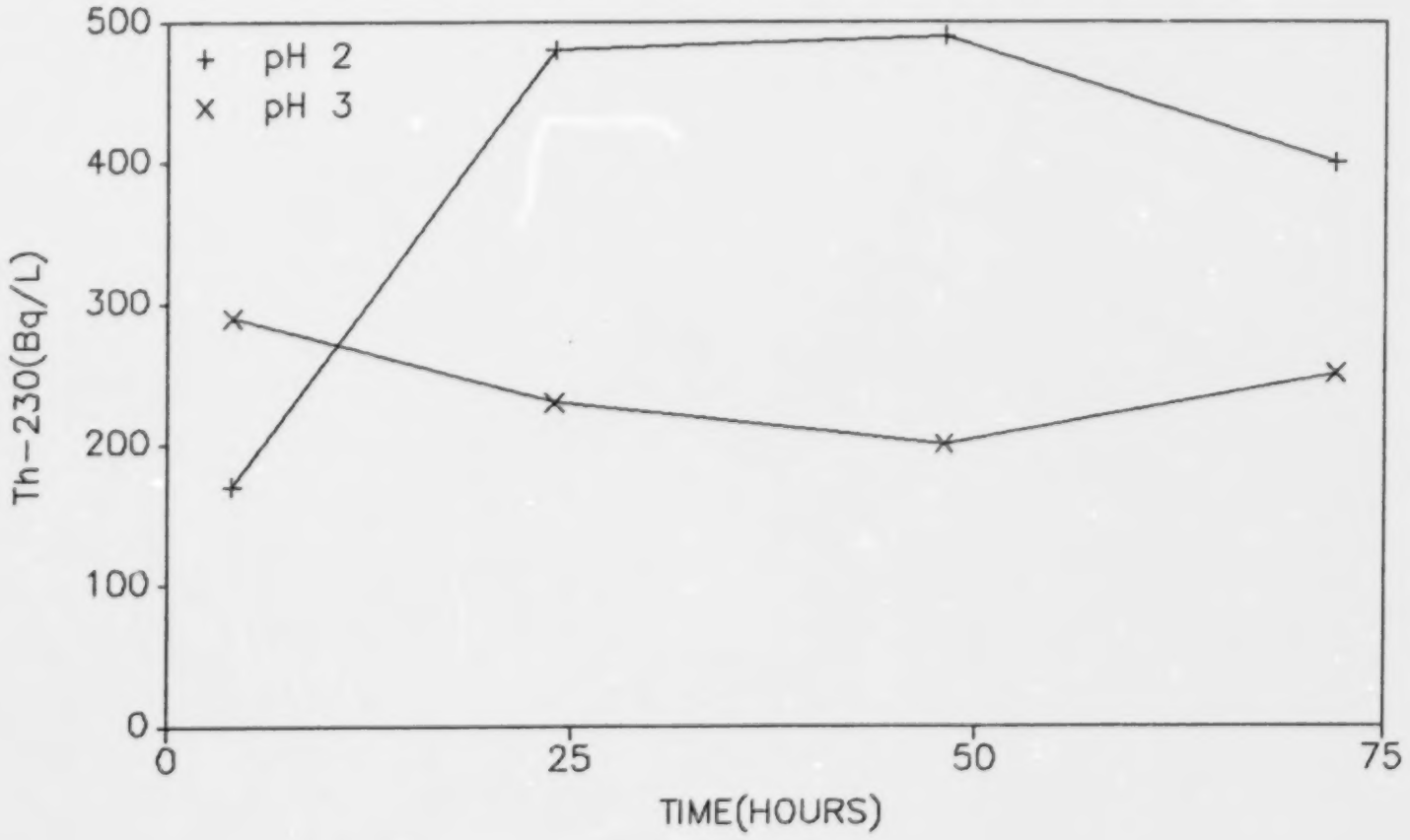

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FIGURE 3-2
pH VARIABILITY TESTS
LEACHATE Th-230 ANALYSIS VS TIME

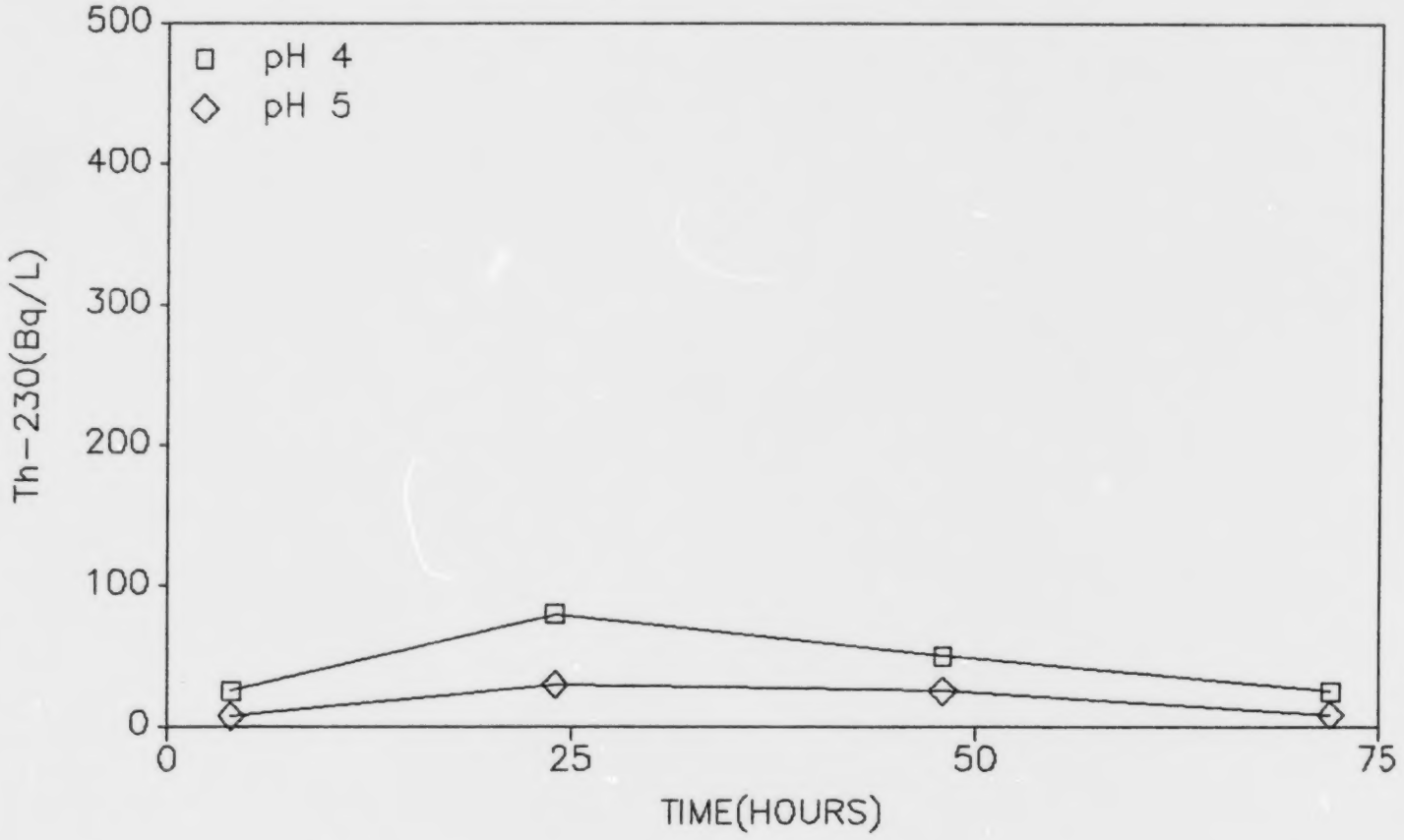

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TABLE 3-6

pH VARIABILITY TESTS (13.5 g/L $FeSO_4$)
LEACHATE AND SOLIDS ANALYSES

Analyte	pH*			
	2	3	4	5
LEACHATE				
Ca (mg/L)	505	505	550	560
SO_4 (mg/L)	12,800	12,800	10,900	10,200
Fe (mg/L)	5,400	5,100	5,000	4,700
Th (mg/L)	23.8	11.0	0.91	0.40
Th-228 (Bq/L)	110	60	5.0	3.0
Th-230 (Bq/L)	350	180	14	11
Th-232 (Bq/L)	110	60	5.0	3.0
Volume (L)	9.1	8.65	8.5	8.4
SOLIDS RESIDUE				
Th (%)	0.0073	0.0110	0.0117	0.0140
Th-228 (Bq/g)	0.35	0.6	0.6	0.7
Th-230 (Bq/g)	0.90	1.3	1.5	2.0
Th-232 (Bq/g)	0.35	0.6	0.6	0.7
Weight (kg)	2.2	2.2	2.2	2.2
CALCULATED HEAD **				
Th (%)	0.0171	0.0153	0.0121	0.0142
Th-228 (Bq/g)	0.8	0.8	0.6	0.7
Th-230 (Bq/g)	2.4	2.0	1.6	2.0
Th-232 (Bq/g)	0.8	0.8	0.6	0.7

* 48-hour leach retention time for pH 2 and pH 3, 30-hour leach retention time for pH 4 and pH 5

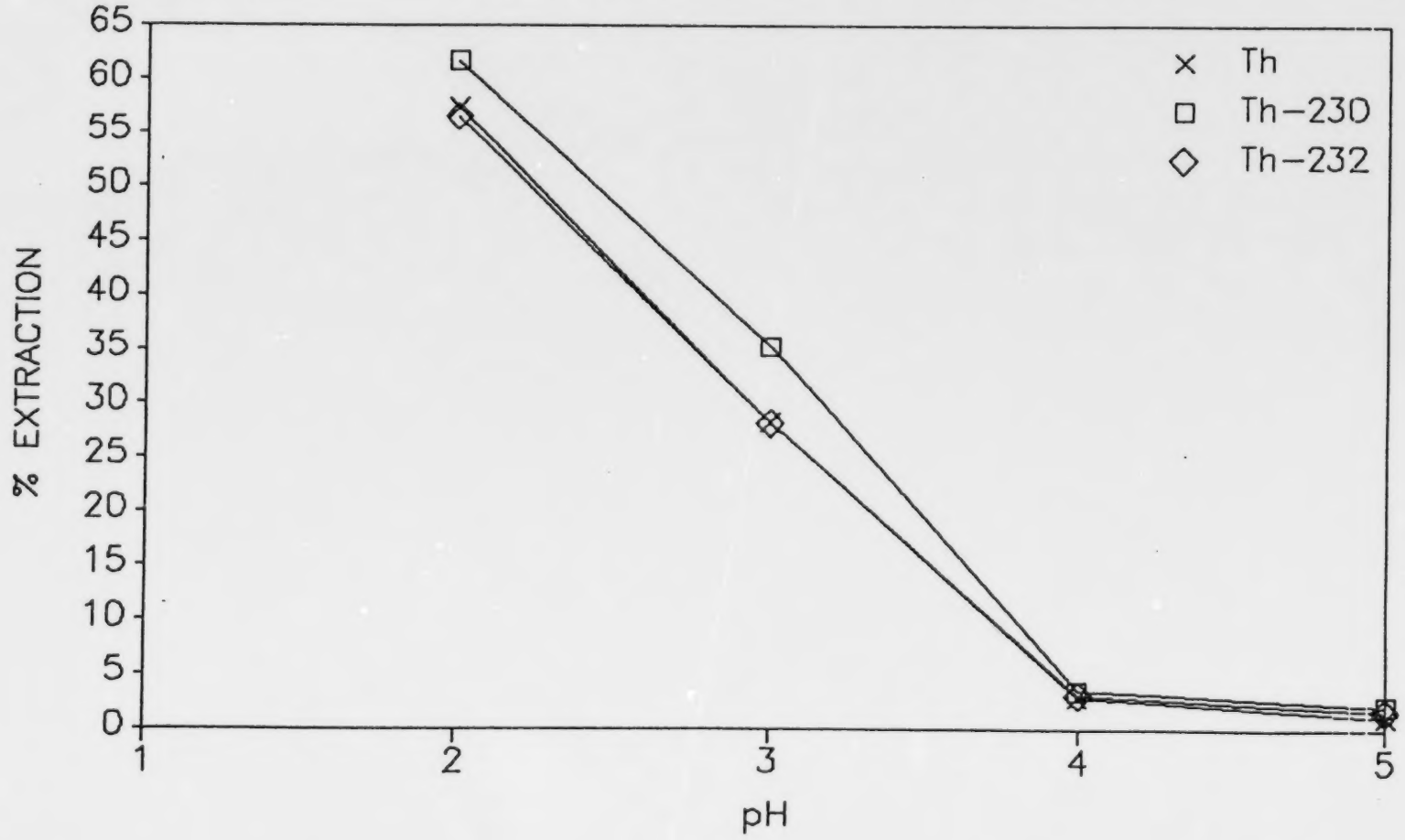
**cf measured head, Table 3-1

TABLE 3-7

pH VARIABILITY TESTS (13.5 g/L $FeSO_4$)
THORIUM EXTRACTION EFFICIENCIES

pH	% Extraction Th	Th-230	Th-232
2	57.4	61.7	56.5
3	28.3	35.3	28.2
4	2.9	3.5	3.1
5	1.1	2.1	1.6

FIGURE 3-3
pH VARIABILITY TESTS(13.5 g/L FeSO4)
THORIUM EXTRACTION EFFICIENCIES



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3.5 FERROUS SULPHATE VARIABILITY TESTS

3.5.1 Methodology

The effect of ferrous sulphate concentration on the re-dissolution of thorium, thorium-230 and thorium-232 from the tailings solids was investigated by performing leach tests at four $FeSO_4$ concentrations with a constant pH of 3.5. The four concentrations used were 21.8, 10.9, 2.7 and 1.35 g/L $FeSO_4$ made up with chemical grade $FeSO_4.7H_2O$ reagent. The test methodology was analogous to the procedure used in the pH variability tests.

The first test run included four leach tests with sampling times of 4,8,16 and 40 hours in order to determine the time required to achieve maximum extraction for each $FeSO_4$ concentration. A total of 1.1 kg of tailings solids was leached with 4.4 L of $FeSO_4$ solution at each of the concentrations specified above. The pH was adjusted to 3.5 with 50 g/L H_2SO_4 solution. The pH tended to drift upwards during the test such that small amounts of acid had to be added during the 40-hour leach to maintain a constant pH. Samples of slurry were withdrawn by a peristaltic pump to afford leachate solution for thorium-230 analysis at each of the specified reaction times.

Using the optimum leaching time determined for each $FeSO_4$ concentration (see section 3.5.2) the four leach tests were repeated with 2.2 kg of tailings solids and 8.8 L of $FeSO_4$ solution. A 46-hour leach time was used for the 21.8 g/L and 10.9 g/L $FeSO_4$ solutions and a 22-hour leach time was used for the 2.7 and 1.35 g/L $FeSO_4$ solutions. The pH in all four tests tended to drift upwards such that periodic additions of acid were required during the leach to maintain a constant pH of 3.5 in the leach slurry. At this pH there would be minor acid consumption occurring during the leach due to reactions with ore minerals present in the tailings solids.

At the end of the leach period the slurry was flocculated and filtered to collect the leachate solution. The solids were washed with water and submitted for analysis. A portion of the leachate was filtered through a 3 micron millipore filter for analysis and the remainder was retained for the leachate oxidation tests.

3.5.2 Results

The test results at varying leach retention times for the four $FeSO_4$ concentrations are given in Table 3-8. The thorium-230 assays are depicted graphically in Figures 3-4 and 3-5.

The behaviour of thorium-230 in leach solutions of varying $FeSO_4$ concentration was different to the behaviour observed in the pH variability tests (refer to Figure 3-1 and Figure 3-2). A gradual decrease of thorium-230 concentration with increasing leach retention time was only observed with the two lower $FeSO_4$ concentrations, 1.35 g/L and 2.7 g/L $FeSO_4$. A leach time of 22 hours was selected for these two concentrations based on the graphical results shown in Figures 3-4 and 3-5.

The two higher concentrations of $FeSO_4$, 10.9 g/L and 21.8 g/L $FeSO_4$, did not reach maximum thorium-230 concentrations in the leachate after 40 hours but a 2-day leach period, actually 46 hours, was selected as an adequate leach time for the subsequent batch leach test at these two $FeSO_4$ concentrations.

The results of the batch leach tests with fixed leach times are presented in Table 3-9 for the four different $FeSO_4$ concentrations at a constant pH of 3.5. Calcium concentrations in the leachate were relatively constant for all four tests. The sulphate and iron levels varied according to the concentration of ferrous sulphate used in each test. The thorium and thorium isotope analyses decreased with decreasing $FeSO_4$ concentrations.

Material balances based on the product analyses given in Table 3-9 for each of the four tests provide the effective extraction of thorium, thorium-230 and thorium-232 from tailings solids under different concentrations of ferrous sulphate leach solution. The calculated percent extraction values for 21.8, 10.9, 2.7 and 1.35 g/L $FeSO_4$ solution at a constant pH of 3.5 are given in Table 3-10 and depicted in Figure 3-6.

These results show that the ratio of extracted thorium: thorium-230: thorium-232 remains approximately constant at each $FeSO_4$ concentration and

TABLE 3-8

$FeSO_4$ VARIABILITY TESTS (pH 3.5)
LEACHATE THORIUM ANALYSIS AT DIFFERENT REACTION TIMES (Bq/L)

Analyte	Leach Time (h)	$FeSO_4$ Concentration (g/L) 21.8	10.9	2.7	1.35
Th-228	4	3.5	0.9	0.7	0.55
	8	13	4.5	1.0	0.45
	16	13	10	4.0	2.5
	40	14	13	1.1	0.9
Th-230	4	20	4.5	3.0	2.5
	8	70	20	8.0	2.5
	16	60	40	12	6.0
	40	80	55	5.5	4.0
Th-232	4	3.5	0.9	0.7	0.55
	8	13	4.5	1.0	0.45
	16	13	10	4.0	2.5
	40	14	13	1.1	0.9

FIGURE 3-4
FeSO4 VARIABILITY TESTS
LEACHATE ANALYSIS VS TIME

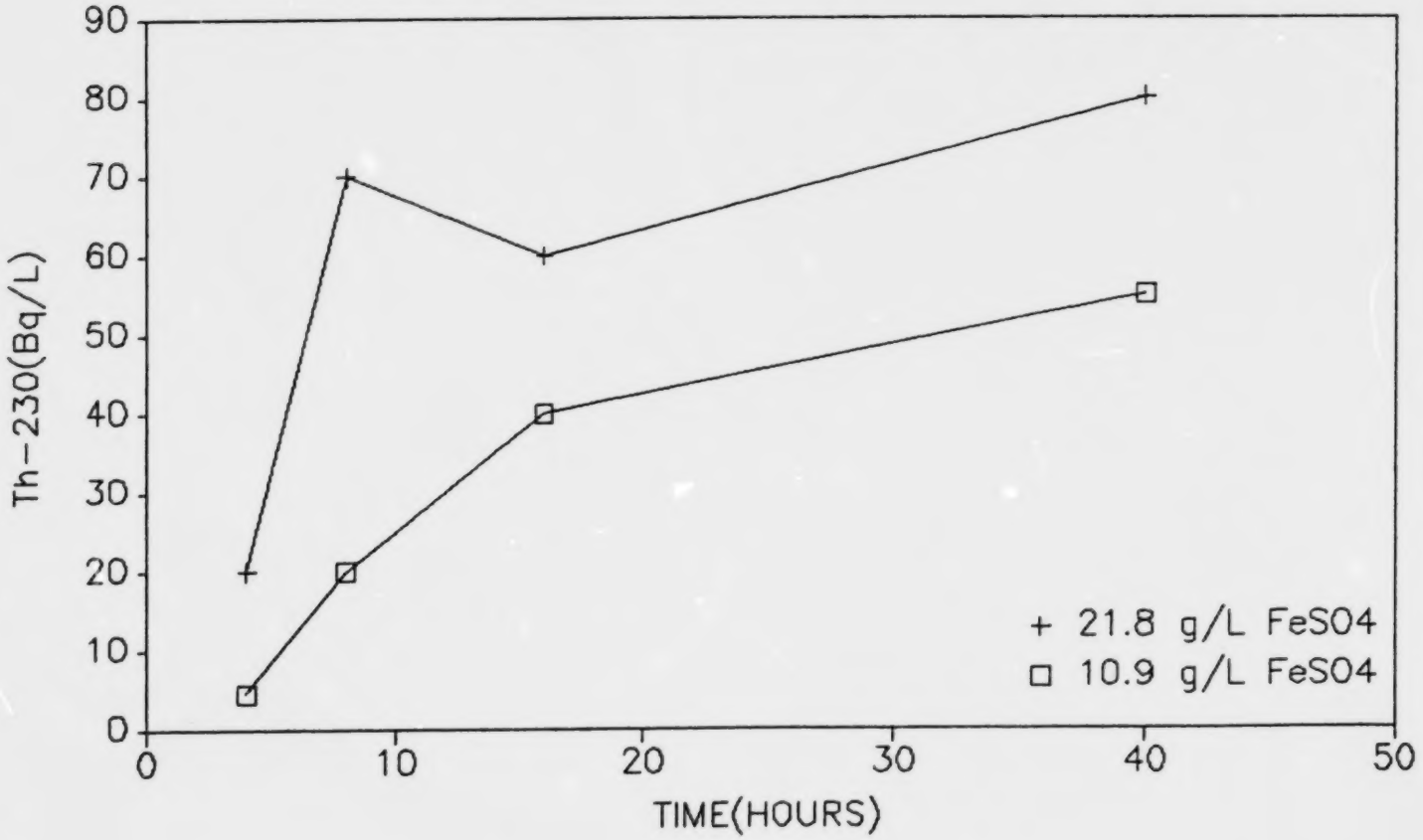

FIGURE 3-5
FeSO4 VARIABILITY TESTS
LEACHATE ANALYSIS VS TIME

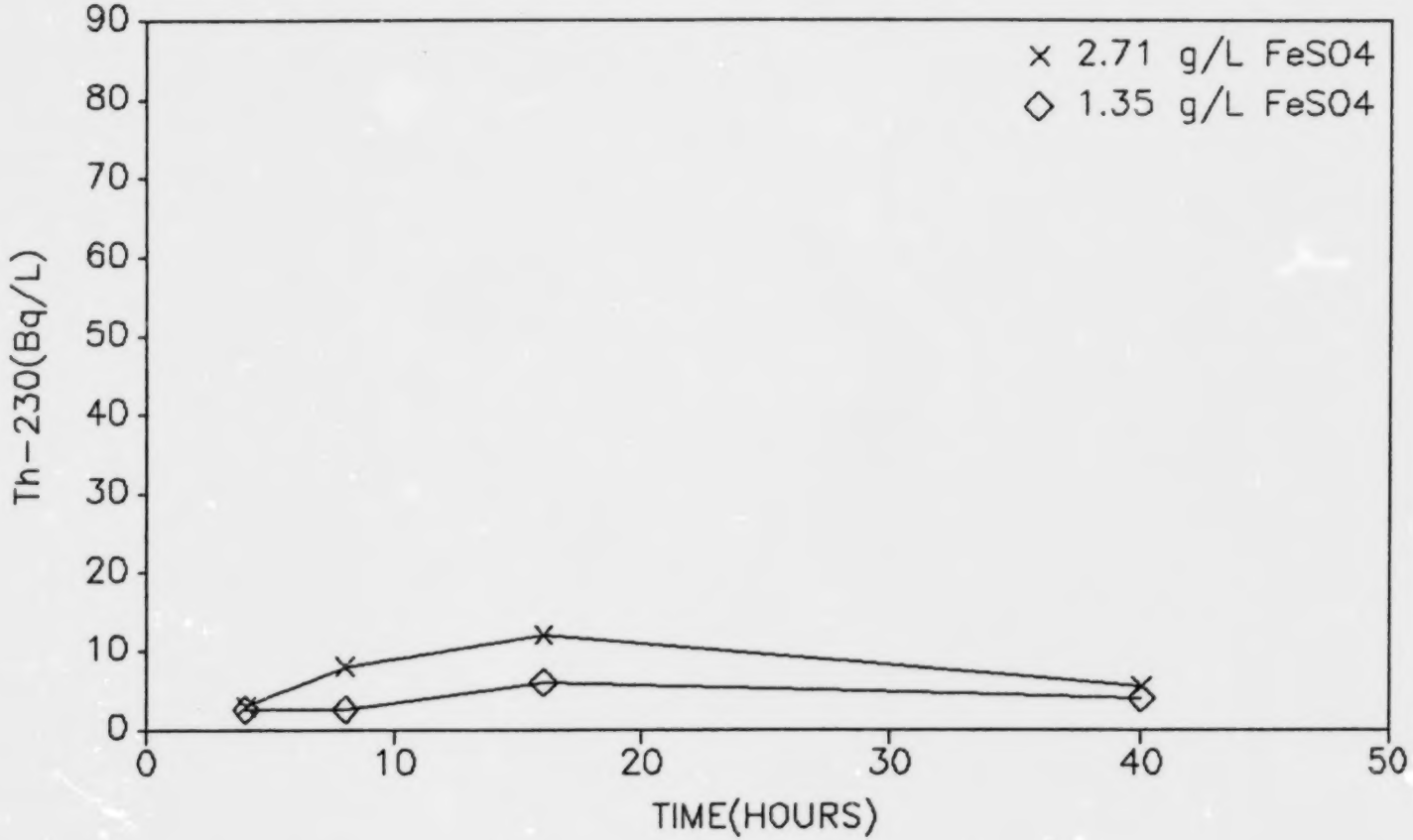

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TABLE 3-9

$FeSO_4$ VARIABILITY TESTS (pH 3.5)
LEACHATE AND SOLIDS ANALYSES

Analyte	$FeSO_4$ Concentration (g/L)*			
LEACHATE	**21.8**	**10.9**	**2.7**	**1.35**
Ca (mg/L)	560	560	540	560
SO_4 (mg/L)	16,000	9,100	3,600	2,900
Fe (mg/L)	7,450	3,900	930	485
Th (mg/L)	11.9	6.5	2.05	1.45
Th-228 (Bq/L)	60	20	10	4.5
Th-230 (Bq/L)	180	80	25	11
Th-232 (Bq/L)	60	20	10	4.5
Volume (L)	8.39	8.33	8.13	8.37
SOLIDS RESIDUE				
Th (%)	0.0151	0.0187	0.0175	0.0219
Th-228 (Bq/g)	0.60	0.9	0.8	1.0
Th-230 (Bq/g)	1.9	2.5	2.5	3.5
Th-232 (Bq/g)	0.60	0.9	0.8	0.9
Weight (kg)	2.2	2.2	2.2	2.2
CALCULATED HEAD**				
Th (%)	0.0196	0.0212	0.0182	0.0227
Th-228 (Bq/g)	0.8	1.0	0.8	1.0
Th-230 (Bq/g)	2.6	2.8	2.6	3.5
Th-232 (Bq/g)	0.8	1.0	0.8	1.0

* 46-hour leach retention time for 21.8 g/L and 10.9 g/L $FeSO_4$ concentration, 22-hour leach retention time for 2.7 g/L and 1.35 g/L $FeSO_4$ concentration

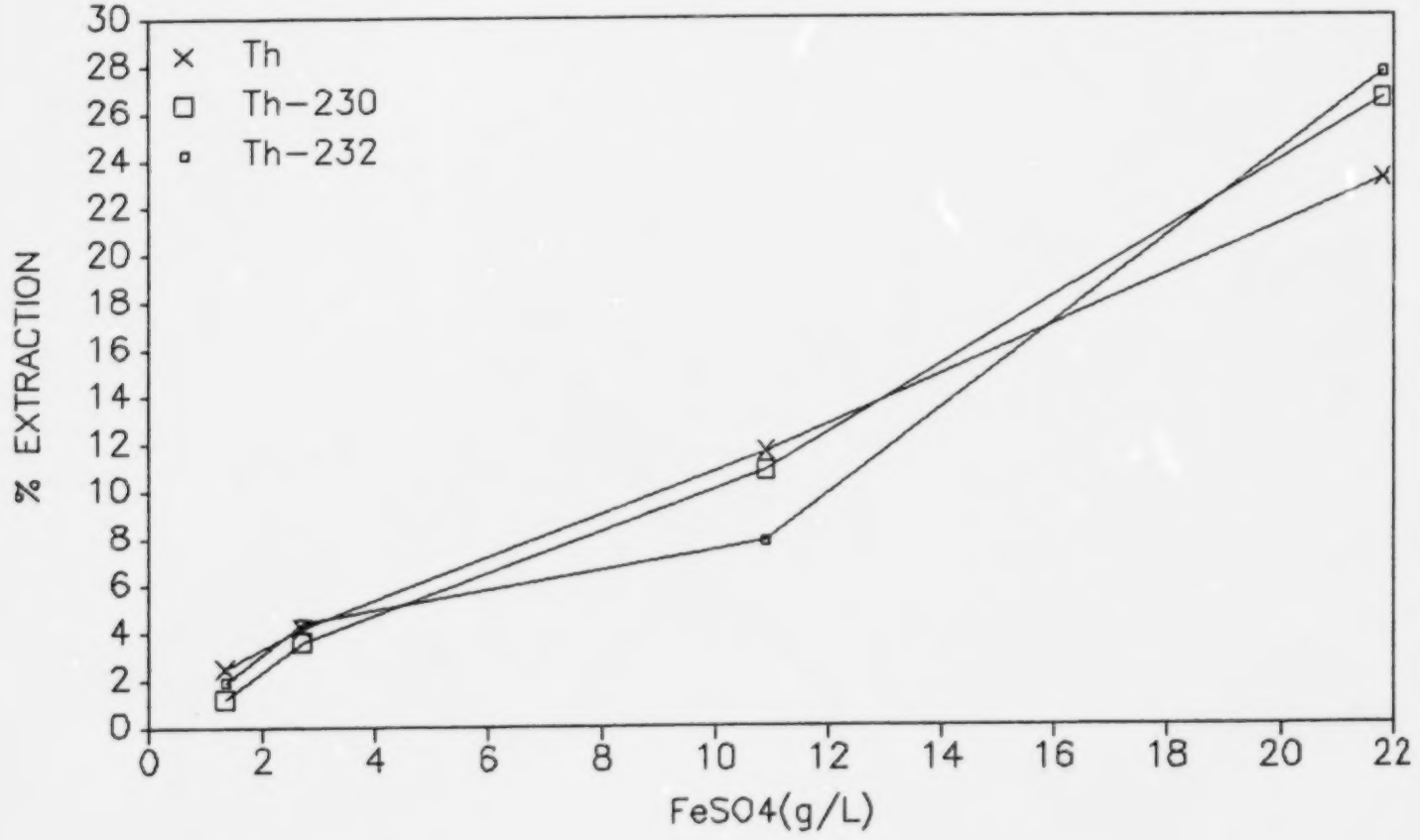
**cf. measured head, Table 3-1

TABLE 3-10

$FeSO_4$ VARIABILITY TESTS (pH 3.5)
THORIUM EXTRACTION EFFICIENCIES

$FeSO_4$ Concentration (g/L)	% Extraction Th	Th-230	Th-232
21.8	23.1	26.5	27.6
10.9	11.6	10.8	7.8
2.7	4.2	3.6	4.4
1.35	2.5	1.2	1.9

FIGURE 3-6
FeSO4 VARIABILITY TESTS
THORIUM EXTRACTION VS g/L FeSO4



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that the extraction of all three increase with increasing $FeSO_4$ concentration. The maximum thorium extraction achieved was approximately 25% with the 21.8 g/L $FeSO_4$ concentration. A comparison of these results with the pH variability results given in Table 3-7 shows good agreement between the two sets of experiments. That is, the ratio of thorium isotopes in extracts and residues remain relatively constant with pH or $FeSO_4$ concentration variation. The graphical presentation shown in Figure 3-6 indicates that there is a linear relationship between thorium extraction and ferrous sulphate concentration within the range of $FeSO_4$ concentrations used in the tests.

3.6 LEACHATE OXIDATION TESTS

3.6.1 Methodology

The leachate solutions produced in the batch pH and $FeSO_4$ variability tests were subjected to oxidation tests to determine the extent of thorium and thorium-230 re-precipitation with pH adjusted leachate under oxidizing conditions.

The remaining volumes of leachate from the four pH variability leach tests and from the four $FeSO_4$ variability leach tests were adjusted to pH 4 with lime in 20 L plastic pails using mechanical mixing. Excess hydrogen peroxide (50% H_2O_2) was added to each leachate to ensure complete oxidation of the ferrous iron to ferric iron. Excess H_2O_2 was evident from the effervescence noticed in the leachate. It was also checked by the starch paper/KI solution test.

The eight oxidized leachate solutions were allowed to stand for two weeks at pH 4. The oxidizing reaction:

$$FeSO_4 + H_2O_2 + H_2O \text{ ----> } Fe_2O_3 + 2H_2SO_4$$

generated sulfuric acid which necessitated periodic lime addition during the two-week period to maintain a constant pH of 4.

At the end of the two-week period the complete slurry was filtered to collect a filtrate and a precipitate for each leachate oxidation test. Both the filtrate and precipitate were submitted for analysis to provide a material balance for the pH variable leachate oxidation tests and for the $FeSO_4$ variable leachate oxidation tests.

3.6.2 Results

The analytical results and calculated head for the pH variable leachate oxidation tests are presented in Table 3-11. Precipitation efficiencies for each of the four tests are summarized in Table 3-12. These have been calculated based on the filtrate and precipitate product analysis given in Table 3-11.

TABLE 3-11

pH VARIABILITY TESTS (13.5 g/L $FeSO_4$)
LEACHATE OXIDATION TEST RESULTS

Analyte	pH			
FILTRATE	**2**	**3**	**4**	**5**
Ca (mg/L)	560	590	690	630
SO_4 (mg/L)	3,780	2,320	1,720	1,720
F (mg/L)	870	290	0.27	0.20
T (mg/L)	0.1	0.0017	<0.0001	<0.0001
Th-228 (Bq/L)	0.30	0.11	0.03	0.02
Th-230 (Bq/L)	3.0	0.35	0.20	0.20
Th-232 (Bq/L)	0.30	0.11	0.03	0.02
Volume (L)	8.1	7.65	7.5	7.4
PRECIPITATE				
Ca	18.0	21.0	14.0	19.0
SO_4 (%)	40.0	31.7	41.3	51.5
Fe (%)	19.0	18.0	23.0	10.0
Th (%)	0.105	0.039	0.0055	0.00085
Th-228 (Bq/g)	3.5	0.80	0.25	0.07
Th-230 (Bq/g)	16	3.0	0.90	0.25
Th-232 (Bq/g)	3.5	0.80	0.25	0.07
Weight (g)	217.4	248.15	210.6	180.4
CALCULATED HEAD				
Th (mg/L)	28.2	12.7	1.5	0.2
Th-228 (Bq/L)	94	26	7.0	1.7
Th-230 (Bq/L)	432	98	25	6.1
Th-232 (Bq/L)	94	26	7.0	1.7

TABLE 3-12

pH VARIABILITY TESTS (13.5 g/L $FeSO_4$)
LEACHATE OXIDATION PRECIPITATION EFFICIENCIES

	Precipitation Efficiency (%)					
pH	Ca	SO_4	Fe	Th	Th-230	Th-232
2	89.6	74.0	85.4	99.7	99.3	99.7
3	92.0	81.6	95.3	>99.9	99.6	99.6
4	85.1	87.1	>99.9	>99.9	99.2	99.6
5	88.0	88.0	>99.9	>99.9	96.8	98.8

The calcium precipitation efficiency includes the calcium added as lime in the pH 4 adjustment step. Sulphate removal from the leachate increases from pH 2 to pH 5 but is limited by the solubility of gypsum in the filtrate. Thorium removal from the leachate is virtually complete for all four tests. It does not appear to be controlled by either iron or sulphur precipitation.

The analytical results and calculated head for the $FeSO_4$ variable leachate oxidation tests are summarized in Table 3-13. Precipitation efficiencies, calculated from product analyses, are given in Table 3-14.

Since calcium and sulphate precipitation are limited by gypsum solubility the calculated removal efficiency for these two species is higher for the tests with higher $FeSO_4$ concentration. Iron and thorium removal is virtually complete in all four tests.

TABLE 3-13

$FeSO_4$ VARIABILITY TESTS (pH 3.5)
LEACHATE OXIDATION TEST RESULTS

Analyte	$FeSO_4$ Concentration (g/L $FeSO_4$)			
FILTRATE	**21.8**	**10.9**	**2.7**	**1.35**
Ca (mg/L)	600	660	720	660
SO_4 (mg/L)	2,210	2,050	2,070	2,090
Fe (mg/L)	150	0.64	25	1.3
Th (mg/L)	0.04	0.02	0.05	0.03
Th-228 (Bq/L)	0.25	0.25	0.20	0.35
Th-230 (Bq/L)	0.90	0.80	0.90	0.70
Th-232 (Bq/L)	0.25	0.25	0.20	0.35
Volume (L)	7.385	7.33	7.13	7.37
PRECIPITATE				
Ca (%)	13.0	11.0	12.0	12.0
SO_4 (%)	36.5	36.7	32.6	37.0
Fe (%)	20.0	18.0	20.0	20.0
Th (%)	0.032	0.027	0.035	0.047
Th-228 (Bq/g)	1.3	1.1	1.6	2.0
Th-230 (Bq/g)	5.0	4.0	5.5	7.5
Th-232 (Bq/g)	1.3	1.1	1.6	2.0
Weight (g)	220.9	174.4	38.3	24.55
CALCULATED HEAD				
Th (mg/L)	9.6	6.4	1.9	1.6
Th-228 (Bq/L)	39	26	9	7
Th-230 (Bq/L)	150	96	30	26
Th-232 (Bq/L)	39	26	9	7

TABLE 3-14

$FeSO_4$ VARIABILITY TESTS (pH 3.5)
LEACHATE OXIDATION PRECIPITATION EFFICIENCIES

$FeSO_4$ Concentration (g/L)	Precipitation Efficiency (%)					
	Ca	SO_4	Fe	Th	Th-230	Th-232
21.8	86.6	83.2	97.5	99.6	99.4	99.4
10.9	79.9	85.3	>99.9	99.7	99.2	99.1
2.7	47.3	45.8	97.7	99.7	97.1	99.7
1.35	37.7	37.1	99.8	98.1	97.3	95.0

3.7 LYSIMETER TESTS

3.7.1 Methodology

The thorium dissolution characteristics observed in the batch leach tests were investigated under column leaching conditions in a series of lysimeter tests.

A total of four different leaching solutions were used in the column leach tests. Two of the solutions contained 13.5 g/L $FeSO_4$ with one solution having a pH corresponding to the pH which gave maximum thorium leaching and the second solution having a pH which gave the minimum thorium extraction. The other two solutions were at pH 3.5, one with a $FeSO_4$ concentration corresponding to the concentration which gave maximum thorium leaching and the other with the $FeSO_4$ concentration which gave minimum thorium leaching.

From the batch leach test results the four leach solutions used in the lysimeter tests were therefore:

- 13.5 g/L $FeSO_4$ at pH 2
- 13.5 g/L $FeSO_4$ at pH 5
- 21.8 g/L $FeSO_4$ at pH 3.5
- 1.35 g/L $FeSO_4$ at pH 3.5.

In the first series of lysimeter tests 6.33 kg (dry basis) of tailings were placed in a 10 cm diameter column to provide a 4 L bed volume (BV) of tailings. The tailings solids were supported in the column by glass fiber and a stainless steel screen. The appropriate leach solution was then pumped to the top of the tailings bed via a peristaltic pump from a 20 L plastic pail reservoir. The flowrate at the start of the test was approximately 50 mL/min but it decreased with time to as low as 30 mL/min. A total of 40 L or 10 bed volumes of solution were passed through each of the four columns.

The next set of parallel experiments were supposed to be run at a flowrate of 30 mL/min but the tailings bed in each column began to plug up and flowrates decreased to 10 mL/min during the first bed volume of flow through the

column. It was noticed that tapping of the column to consolidate the bed seriously affected the flow through the bed. It was then rationalized that the higher 60 mL/min flowrates achieved in the first set of experiments were likely due to channelling of the solution in the columns which in turn would have resulted in poor solution contact with the complete tailings bed. The erratic nature of the analyses obtained in the first set of leach tests seem to confirm that solution channelling had occurred in the columns.

It was then decided to reduce the bed volume of tailings solids to 1 L by placing 1.395 kg (dry basis) of tailings in the 10 cm column giving a bed height of approximately 13 cm. The tailings bed in each column was consolidated by tapping the outside of the column before introducing any leach solution. This change in lysimeter conditions gave a maximum flowrate of 20 mL/min through the bed which decreased slightly by the end of the test.

The effect of percolation flowrate on thorium dissolution was investigated by reducing the maximum flow by half to 10 mL/min and then by another half to 5 mL/min. The three flowrates used in the lysimeter tests were therefore:

- 20 mL/min (0.153 $m^3/h/m^2$)
- 10 mL/min (0.076 $m^3/h/m^2$)
- 5 mL/min (0.038 $m^3/h/m^2$).

A total of twelve separate lysimeter tests were completed to provide experimental data for geochemical modelling. Four different leach solutions were passed through the tailings bed at the three different flowrates. The leachate discharge from the bed was collected and the first, third, sixth and tenth bed volume submitted for thorium analysis after filtration through a 3 micron millipore filter.

3.7.2 Results

Analytical results from the 20, 10 and 5 mL/min lysimeter tests are given in Tables 3-15, 3-16 and 3-17. A total of 10 L of solution (10 bed volumes) were passed through each column at each of the three flowrates to provide the required experimental data. The results previously obtained in the batch leach tests were generally confirmed in the lysimeter tests although leaching

TABLE 3-15

LYSIMETER TEST RESULTS - 20 mL/min
LEACHATE ANALYSIS

			mg/L	Bq/L		
pH	$FeSO_4$ (g/L)	BV	Th	Th-228	Th-230	Th-232
2	13.5	1	0.25	1.0	6.5	1.0
5	13.5	1	0.05	0.35	0.90	0.35
3.5	21.8	1	0.025	0.25	0.60	0.25
3.5	1.35	1	0.010	0.07	0.25	0.07
2	13.5	3	0.17	0.7	4.5	0.7
5	13.5	3	0.013	0.20	0.80	0.20
3.5	21.8	3	0.060	0.50	1.2	0.50
3.5	1.35	3	0.0035	0.05	0.11	0.05
2	13.5	6	0.004	0.04	0.5	0.04
5	13.5	6	0.016	0.16	0.35	0.16
3.5	21.8	6	0.46	3.0	7.5	3.0
3.5	1.35	6	0.0025	0.19	0.35	0.19
2	13.5	10	0.006	0.07	0.80	0.07
5	13.5	10	0.010	0.19	0.55	0.19
3.5	21.8	10	0.52	2.5	8.0	2.5
3.5	1.35	10	0.0005	0.11	0.65	0.11

TABLE 3-16

LYSIMETER TEST RESULTS - 10 mL/min
LEACHATE ANALYSIS

			mg/L	Bq/L			
pH	$FeSO_4$ (g/L)	BV	Th	Th-228	Th-230	Th-232	pH
2	13.5	1	23.8	50	220	50	2.8
5	13.5	1	0.045	0.20	0.70	0.20	3.8
3.5	21.8	1	0.045	0.30	1.1	0.30	3.3
3.5	1.35	1	0.0019	0.03	0.11	0.03	5.4
2	13.5	3	12.5	45	200	45	2.0
5	13.5	3	0.035	0.15	0.90	0.15	4.1
3.5	21.8	3	0.045	0.25	1.1	0.25	4.1
3.5	1.35	3	0.001	0.03	0.13	0.03	5.1
2	13.5	6	7.65	30	120	30	2.1
5	13.5	6	0.015	0.12	0.55	0.12	3.9
3.5	21.8	6	0.34	0.13	5.5	0.13	3.6
3.5	1.35	6	0.003	0.35	1.5	0.35	4.5
2	13.5	10	5.76	20	90	20	2.1
5	13.5	10	0.04	0.17	0.20	0.17	3.8
3.5	21.8	10	3.04	12	45	12	3.9
3.5	1.35	10	0.0011	0.02	0.11	0.02	4.5

TABLE 3-17

LYSIMETER TEST RESULTS - 5 mL/min
LEACHATE ANALYSIS

pH	$FeSO_4$ (g/L)	BV	mg/L Th	Bq/L Th-228	Bq/L Th-230	Bq/L Th-232	pH
2	13.5	1	6.4	30	140	30	-
5	13.5	1	0.019	0.20	3.0	0.20	-
3.5	21.8	1	0.018	0.30	1.2	0.30	-
3.5	1.35	1	0.011	0.04	0.35	0.04	-
2	13.5	3	27.7	90	470	90	2.1
5	13.5	3	0.0085	0.20	0.70	0.20	3.4
3.5	21.8	3	0.016	0.30	0.70	0.30	3.3
3.5	1.35	3	0.0045	0.07	0.6	0.07	4.2
2	13.5	6	10.3	35	160	35	1.9
5	13.5	6	0.007	0.08	0.35	0.08	3.3
3.5	21.8	6	1.18	5.0	16	5.0	3.3
3.5	1.35	6	0.0012	0.05	0.25	0.05	4.1
2	13.5	10	2.17	8.5	40	8.5	1.9
5	13.5	10	0.0065	0.11	0.45	0.11	3.4
3.5	21.8	10	3.42	13	50	13	3.3
3.5	1.35	10	0.001	0.04	0.16	0.04	4.0

rates and efficiencies for the lysimeter tests were, as expected, less than those observed in the batch leach tests.

The highest thorium concentrations were observed in the leachate from the pH 2, 13.5 g/L $FeSO_4$ test. The lowest leachate concentrations were observed in the pH 3.5, 1.35 g/L $FeSO_4$ test. It was evident from the results that a greater number of bed volumes would have been required to allow the dissolution reactions to go to completion under lysimeter test conditions.

In the pH 2, 13.5 g/L $FeSO_4$ test thorium concentrations were high for the 5 and 10 mL/min tests with a decrease in concentration being observed with increasing bed volumes. Although lower concentrations were expected for the 20 mL/min test, due to less leachate retention time in the column, the very low levels obtained for this test were likely due to solution channelling effects. Hence the 20 mL/min results should be disregarded during the assessment of the test data.

In the pH 5, 13.5 g/L $FeSO_4$ test the low concentrations observed at all three flowrates decreased with increasing bed volumes.

In the pH 3.5, 21.8 g/L $FeSO_4$ test there was an increase in leachate concentration with increasing bed volumes which indicated a gradual increase in reactivity of the solution with the tailings.

In the pH 3.5, 1.35 g/L $FeSO_4$ test the low leachate thorium concentrations gradually decreased with increasing bed volumes for the 5 and 20 mL/min test but showed very little variation in the 10 mL/min test. The low leachate concentrations in these tests suggested that little thorium dissolution would have taken place even with extended bed volumes.

Estimates of total leaching efficiency for each lysimeter test were calculated by interpolating the leachate analysis for the first, third, sixth and tenth bed volume to arrive at estimates of thorium analysis for the other six bed volumes collected for each test. Comparison of the total thorium content in the 10 L of leachate to the thorium originally present in the tailings

solids therefore gave an approximate thorium leach efficiency for each lysimeter test. These estimates can only be used as a guide since the actual thorium content in the tailings feed to each column would have varied between columns. Also, the relative efficiencies for tests with slower kinetics could differ appreciably in longer-term tests. Study cost and time restrictions did not allow for complete mass balances to be done for each lysimeter test.

Interpolation of bed volume analysis and leach efficiency calculations for the twelve lysimeter tests are detailed in Appendix B. The estimated thorium extractions for each lysimeter test, as calculated from the interpolated test results, are summarized in Table 3-18.

Noticeable thorium extractions were only observed for the conditions which gave the maximum thorium extractions in the batch leach tests, namely the pH 2, 13.5 g/L $FeSO_4$ test and the pH 3.5, 21.8 g/L $FeSO_4$ test. For these two tests thorium extractions generally increased with decreasing flowrates through the tailings bed as a result of longer leachate retention time at lower flowrates. Only the pH 2, 13.5 g/L $FeSO_4$ column test approached the thorium extractions observed in the batch leach tests with approximately 55% extraction being achieved for both thorium and thorium-232.

TABLE 3-18

ESTIMATED LYSIMETER TEST EXTRACTION EFFICIENCIES*

pH	$FeSO_4$ (g/L)	Flowrate (mL/min)	% Extraction Th	% Extraction Th-230
2	13.5	20	0.4**	0.7**
2	13.5	10	50.1	41.7
2	13.5	5	54.0	56.0
5	13.5	20	0.09	0.17
5	13.5	10	0.14	0.21
5	13.5	5	0.04	0.23
3.5	21.8	20	1.4	1.4
3.5	21.8	10	3.6	3.3
3.5	21.8	5	5.9	5.2
3.5	1.35	20	0.02	0.10
3.5	1.35	10	0.01	0.14
3.5	1.35	5	0.02	0.09

* cumulative extraction for ten bed volumes of eluant, based on interpolated results given in Appendix B

**low extractions likely due to solution channelling

3.8 ANALYTICAL QUALITY ASSURANCE PROGRAM

An analytical quality assurance program was incorporated into the study at the request of Dr. H. Steger of CANMET. A total of 21 reference standards, with CANMET identification numbers, were submitted directly to the Saskatchewan Research Council for analysis during the course of the testwork. These liquid standards were interspersed for analysis with the samples generated during the test program.

All 21 reference standards were analysed for Thorium-230 and a total of 16 standards were analysed for total thorium. Iron, sulphate, and calcium analyses were performed on 5 of the 21 reference standards. The analytical results are listed in Table 3-19.

The SRC analytical methods used for Thorium-230 and Thorium-232 are given in Appendix C. The detection limit for Th-230 is 0.01 Bq/g with 10% precision in the 0.18-0.37 Bq range and 5% precision for thorium-230 contents greater than 0.37 Bq. The detection limit for Th-232 is 0.0002 mg/L with a 5% precision for levels greater than 0.010 mg/L.

TABLE 3-19

QUALITY CONTROL REFERENCE STANDARDS-ANALYTICAL RESULTS

Sample No.	Th (mg/L)	Th-230 (Bq/L)	Fe (mg/L)	SO_4 (mg/L)	Ca (mg/L)
1	0.103	3.0			
2	0.623	2.0	420	1,030	430
3	1.860	2.5			
4	0.0009	0.05			
5	0.011	7.5			
6	1.980	4.0			
7	2.180	18			
8	1.960	12			
9	0.110	3.5	46	442	100
10	0.0001	<0.02			
11	4.860	6.5			
12	0.110	3.5			
13	5.240	14			
14	0.001	0.04			
15		17			
16		2.0			
17		8.0	240	1,060	410
18	0.0005	<0.02			
19	1.810	6.5	400	1,040	420
20		<0.02			
21		0.04			

4.0 GEOCHEMISTRY OF THORIUM

4.1 OVERVIEW

In minerals, thorium exists invariably as a tetravalent moiety (oxidation state: +4) and, unlike uranium,the thorium ion is not subject to oxidation/reduction under natural conditions in the environment. This implies that the solubility of thorium in the liquid phase depends upon the type of thorium mineral, the pH, and the kinetics of the dissolution reaction. In Elliot Lake tailings, thorium is present as re-precipitated thorium hydroxide [$Th(OH)_4$] and the primary mineral, monazite [(Ce, La, Th, U^{IV}) PO_4]. Of these two thorium minerals, thorium hydroxide is the more abundant. From the rare earth mineral composition of the ore, monazite comprises 5-20% of the thorium inventory in the tailings. Thorium hydroxide is also the more water soluble mineral. The solubility of thorium hydroxide and the complexation of the thorium ion with inorganic ligands has been reviewed by Langmuir and Herman (1980). The relevant reactions and the equilibrium constants are summarized in Table 4.1.

The most obvious feature of the reactions is that at a specified pH value (i.e. hydrogen ion activity), the solubility of thorium oxides may vary over four orders of magnitude (33,000-fold), depending on the crystallinity of the mineral. This unusually high variability has been pointed out by Langmuir and Herman (1980). The pH dependence of solubility is rather complex. At pH values above 4.5 and constant sulphate and ionic strength, the equilibrium concentration of thorium in solution is essentially constant. At lower pH values, the thorium concentration is expected to increase with decreasing pH values. Due to the strong tendency to form sulphato complexes,dissolved thorium is expected to increase significantly with increasing sulphate in solution. In addition, the dissolved thorium in solution is dependent on the ionic strength. This dependence is particularly significant at low pH values.

The thermodynamics of monazite solution equilibrium is not well known. Considering the relative solubility of related minerals such as uranium (IV)

TABLE 4-1

SOLUBILITY EQUILIBRIUM OF THORIUM COMPOUNDS/COMPLEXES

Reaction	Log K
$Th(OH)_4$ (crystalline) + $4H^+ = Th^{+4} + 4H_2O$	1.78
$Th(OH)_4$ (amorphous) + $4H^+ = Th^{+4} + 4H_2O$	6.30
$Th^{+4} + H_2O = Th(OH)^{+3} + H^+$	-3.20
$Th^{+4} + 2H_2O = Th(OH)_2^{+2} + 2H^+$	-6.93
$Th^{+4} + 3H_2O = Th(OH)_3^{+} + 3H^+$	-11.70
$Th^{+4} + 4H_2O = Th(OH)_4^{0}$ (aq) + $4H^+$	-15.90
$Th^{+4} + SO_4^{-2} = Th(SO_4)^{+2}$	5.45
$Th^{+4} + 2SO_4^{-2} = Th(SO_4)^{0}$ (aq)	9.73
$Th^{+4} + H_2PO_4^{-} = ThH_2PO_4^{3+}$	4.52
$Th^{+4} + HPO_4^{-2} = ThHPO_4^{2+}$	10.80
$Th^{+4} + 2HPO_4^{-2} = Th(HPO_4)_2^{0}$	22.80
$H_3PO_4^{0} = H^+ + H_2PO_4^{-}$	-2.20
$H_2PO_4^{-} = H^+ + HPO_4^{-2}$	-7.20
$HPO_4^{-2} = H^+ + PO_4^{-3}$	-12.30

phosphates (Langmuir, 1978) and lanthanum phosphates (Sillen and Martell, 1964), the solubility of monazites should be several orders of magnitude less than the thorium hydroxides. In any case, the solubility product would depend on the molar ratio of rare earth minerals to thorium in the host minerals, which, in turn, is highly site specific.

The solubility product, K_s^o, of thorionate (ThO_2) is defined by the following equation:

$$ThO_2(s) + 2H_2O \text{ ---> } Th^{4+} + 4\ OH^-$$

$$K_s^o = [Th^{4+}][OH^-]^4 \qquad \text{(Eq. 4.1)}$$

The terms $[Th^{4+}]$ and $[OH^-]$ in Equation 4.1 represent the activities of the thorium and hydroxyl ions, respectively. These activities are equivalent to molar concentrations at "zero ionic strength" (infinite dilution). The reported solubility product of thorianite varies from $K_s^o = 10^{-49.7}$ (Baes and Mesmer, 1976) to $K_s^o = 10^{-54.2}$ computed by Langmuir and Herman (1980). It is not clear whether this difference is due to the crystallinity of the solid or the uncertainty of the database. For calculating the pH dependence of the thorianite solubility, it is advantageous to express the solubility product in terms of the hydrogen ion activity $[H^+] = 10^{-14}/[OH^-]$ and defining a stability constant, K_{Th}, as $K_{Th} = 56 + \log K_s^o$.

Noting that K_{Th} is the log of the solubility product, and using equilibrium constants as shown on Table 4.1, the solubility of thorium can be predicted by the following mathematical relationship (SENES, 1986) where thorium hydroxide and thorium sulphate are major complexes controlling solubility:

$$[Th] = \frac{10^{(K_{Th} - 4pH)}}{f^4} \{(1 + f^{7/4}\, 10^{(pH - 3.2)} + f^3\, 10^{(2pH - 6.93)} + f^{15/4}\, 10^{(3pH - 11.7)} + f^4\, 10^{(4pH - 15.9)} + f^4\, 10^{5.45}\, [SO_4^{2-}] + f^6\, 10^{9.73}\, [SO_4^{2-}]^2)) \quad \text{(Eq. 4.2)}$$

where:

$[Th]$ = liquid phase concentration of total thorium (moles/L)

f = activity coefficient for divalent ions

$[SO_4^{2-}]$ = concentration of uncomplexed sulphate (moles/L)

K_{Th} = log of apparent solubility product for thorium hydroxide.

Phosphate may also play an important role in thorium solubility, especially in the 3-6 pH range. If phosphate is present, equation 4.2 is modified to the following expression:

$$[Th] = \text{Eq. 4.2} + \frac{10^{(K_{Th} - 4pH)}}{f^4} \left\{ \frac{f^4 [PO_4] \times 10^{(3.53 + 2pH)}}{A} + \frac{f^2\, [PO_4] \times 10^{(2.32 + pH)}}{A} + \frac{f^8 \times [PO_4]^2 \times 10^{(8.27 + 4pH)}}{A^2} \right\} \quad \text{(Eq.4.3)}$$

where:

$$A = [1 + 10^{(pH - 2.2)} + 10^{(2pH - 9.4)} + 10^{(3pH - 21.6)}]$$

Thorium also forms other inorganic complexes with fluoride, chloride and nitrate but these are not likely to be major contributors to thorium mobility in the high ionic strength tailings waters. Thorium is also known to form colloidal precipitates that may well report as dissolved species in standard filtration tests (Hertz et al., 1965). Organic complexing especially in neutral to alkaline waters can also lead to elevated thorium levels and are often the controlling complexes in natural waters.

4.2 EXPERIMENTAL PROGRAM HIGHLIGHTS

4.2.1 Thorium Extractions/Mineral Composition

Elliot Lake uranium ores are unique in a sense that they contain substantial amounts of thorium. The most abundant thorium minerals in the ore is monazite. Monazites are believed to dissolve only partially during the milling process. Therefore, it has been long suspected that the thorium isotopes occur in several mineral phases in the tailings mass.

On a mass basis, thorium-232 is the dominant thorium isotope in the tailings. Although thorium-230 is a fission product of uranium-238, this thorium isotope is believed to dissolve with the uranium ore during the leaching process and is expected to re-precipitate as a solid solution with thorium-232. Consequently, the tailings solids comprise monazites with relatively low thorium-230 activity and secondary precipitates with substantially higher thorium-230 content.

The extractable (leachable) thorium content of the tailings was evaluated from the Tessier extraction test and the lysimeter studies at pH 2. The experimental data from the Tessier test was used without modification. The procedure for evaluating the extractable total thorium is as follows. First, a mathematical model was developed for expressing the total thorium concentration as a function of bed volume replacement. For example, the concentration of the total thorium in the liquid at pH 2, 13.5 g/L $FeSO_4$, 5 ml/min flow after the initial three volume replacements can be represented by:

$$[Th]_{total} = 29{,}684e^{-0.359(n-3)} \qquad \text{(Eq. 4.4)}$$

where:
$[Th]_{total}$ = total thorium concentration (ug/L)
n = number of volume replacements

Then, the model was integrated between n=3 and n=∞. The thorium extracted prior to the third volume was added to the integral to obtain the total

extractable thorium content. The results of the Tessier and lysimeter tests established the mean extractable total thorium level as 64.2% (standard deviation: 1.7%).

The mean thorium-230/thorium-232 activity ratio in unleached tailings solids was found to be 4.3 6. This activity ratio in leach solutions was highly variable ranging from 3.13 to 10.0 in various leaching tests. No definite trend with the extent of leaching could be established. The mean dissolved thorium-230/thorium-232 ratio was estimated to be 5.72 (median = 5.67) with a standard deviation of 2.04. The apparent enrichment of the liquid with the thorium-230 isotope, although a tentative conclusion at the present, implies the preferential leaching of thorium-230 from the tailings.

Based upon the above observation, the following scenario can be derived. Thorium-230 is originally present as a solid solution [U(Th) O_2 (s)] primarily in uraninite and brannerite. Thorium-232, on the other hand, is contained in monasite (rare earth-thorium phosphate) and, to a lesser extent, in brannerite (titanium-thorium oxide mineral) It has been shown (Chemex 1986) that uraninite is more amenable to acid leaching then either monazite or brannerite.

Approximately 93% of thorium-230 and 74.5% of the thorium-232 dissolves in the mill leaching circuit. The remaining 7% of thorium-230 and 25.5% of thorium-232 are associated with un-modified monazite and brannerite. Upon neutralization with lime, two Th-230/Th-232 precipitates form. The larger fraction (84% of the precipitated Th-232), is leachable under acidic conditions (pH 2 - pH 3). This precipitate largely corresponds to thorianite. The smaller fraction (approx. 16%) may be some other thorium mineral that is not readily amenable to leaching under acidic conditions. The thorium 230/ thorium-232 activity ratio in each type of precipitate is apparently 5.61. The distribution of the thorium minerals in the tailings is illustrated in Table 4-2.

The calculations are shown with initial thorium-230 and thorium-232 activities of 2.7 Bq/g and 0.6 Bq/g, respectively. Approximately 64% of thorium-

TABLE 4-2

LEACHABLE AND NON-LEACHABLE THORIUM MINERALS IN TAILINGS

Mineral Type	Thorium-230		Thorium-232	
	Bq/g	%	Bq/g	%
Monazite	0.189	7.0	0.153	25.5
Non-leachable Precipitate	0.349	12.9	0.062	10.3
Leachable Precipitate	2.162	80.1	0.385	64.2
TOTAL	2.700	100.0	0.600	100.0

232 and 80% of thorium-230 appear to be extractable under acidic conditions. Assuming that the leachable isotopes are distributed homogeneously in the solids, the thorium-230/thorium-232 ratio is expected to be 5.61 in the leach liquid. This compares with an initial ratio of 4.5 in the tailings solids. This slight preferential extraction of thorium-230 is evident in thorium extraction efficiencies at pH values ranging from pH 2 to pH 5 (see Table 3.7). The measured extraction efficiency ratios of 1.09 (pH 2), 1.26 (pH 3), 1.13 (pH 4), and 1.31 (pH 5) compare favourably with the "predicted" ratio of 1.25.

It may be noted from Table 4-2, that the thorium-230/thorium-232 activity ratio should reach an ultimate value of 2.50 when all leachable thorium-230 and thorium-232 solids are dissolved. The experimentally observed ratios were 2.57 at pH 2 after 56.5% extraction (maximum possible value: 64.2%) of thorium-232 (Table 3-6). It is recognized that the above scheme is speculative. Nevertheless it does provide a preliminary model for interpreting the experimental data generated in the study.

4.2.2 Thorium Sulphate Complexing

Sulphate is known to be a primary complexing agent for thorium. In order to assess the effects of sulphate, a series of experiments were conducted at constant pH (3.5) and various sulphate levels. The results of the chemical analysis were then compared with predictions using Equation 4.2. The data agree well with the predictions from Equation 4.2. The major input parameters, pH, ionic strength, sulphate concentration and activity coefficient are summarized on Table 4-3 along with the measured and predicted thorium concentrations.

The best fit for data occurs with the log of apparent solubility product for thorium set at 2.9. At lower thorium concentrations, the model predictions are excellent,however, as concentration increases, the spread in the predicted versus measured data increases. This is most probably due to the slow rate of dissolution of thorium hydroxide which results in non-equilibrium conditions at higher concentrations. This can be visually observed in Figure

TABLE 4-3

THORIUM SOLUBILITY AT VARYING $FeSO_4$ CONCENTRATIONS

pH	Ionic strength moles/L	Sulphate moles/L	f	Total thorium (ug/L) measured	Total thorium (ug/L) predicted from Eq. 4.2*
3.5	0.05	0.025	0.47	1450	1380
3.5	0.067	0.033	0.42	2050	1920
3.5	0.2	0.090	0.32	6500	8260
3.5	0.31	0.162	0.31	11,900	25,000

* for $K_{Th} = 2.9$

3-4 where thorium-230 levels are still slowly increasing after 40 hours of extraction. Using the data for thorium-230 at 4, 16, and 40 hours, the curve can be extrapolated using an inverse linear regression.

At infinity the thorium level is approximately 200 Bq/L or 2.5 times the thorium concentration at 40 hours which agrees well with the Equation 4.2 predictions.

4.2.3 Thorium Solubility With Variable pH

Solution pH is known to be a major factor affecting thorium mobility. A series of experiments were undertaken at high ionic strength (13.5 g/L $FeSO_4$) in which the pH was varied. For these studies,sulphate concentration was maintained constant and contact times of 30 hours at pH 4 and 5 and 48 hours at pH 2 and 3 were employed. The measured thorium concentrations are compared with the theoretical calculated values in Table 4-4.

At pH 2, the solubility is controlled by the thorium inventory. Almost all of the soluble thorium was removed. Therefore, the predicted value of 8.3×10^9 ug/L is meaningless. At pH 3, all of the thorium is not dissolved but this is again likely due to the slow rate of dissolution of thorium minerals which results in equilibrium not being obtained.

At ph 4 and 5, the model underpredicts thorium concentrations. This underprediction likely results from:

- formation of thorium colloids which are not filtered from solution; or
- formation of other complexes.

The formation of colloid precipitates is a plausible mechanism. Evidence of this can be gleaned from Figure 3-5 and from the column lysimeter studies.

In Figure 3-5, it can be seen that at pH levels 4 and 5, thorium tends to leach to a maximum concentration after 16 hours of leaching after which levels decline. This may well be the result of crystal growth or particle

TABLE 4-4

THORIUM SOLUBILITY AT VARYING pH LEVELS

pH	Ionic strength moles/L	Sulphate moles/L	f	Thorium Solubility* (ug/L) measured	predicted
2	0.2	0.09	0.32	23,800	8.3×10^9 (26,800)**
3	0.2	0.09	0.32	11,000	825,000 (25,300)**
4	0.2	0.09	0.32	910	82
5	0.2	0.909	0.32	400	0.01

Notes:

* based upon $K_{Th} = 2.9$

** bracket values are maximum levels with all the Tessier extractable thorium removed.

agglomeration resulting in more of the colloidal thorium being removed by filtration.

The column studies at pH 3.5 and 5 show a similar trend. At lower column flowrates, one would expect to get higher thorium concentrations. However, the thorium concentrations at 5 mL/min are lower than at 10 mL/min. This again suggests that colloidal particles may be more effectively trapped in the columns at lower flow rates. In addition, the column data report dissolved thorium levels one or more orders of magnitude below the batch agitated experiments. This may also inpart be due to filtration of colloidal thorium in columns.

The formation of other thorium complexes may also explain the elevated thorium levels at pH levels of 4 and 5.

The only inorganic complex that is likely to increase thorium solubility at pH 4 and 5 is phosphate. Using equation 4.3 and a K_{Th} of 2.9 at pH 4, the thorium concentration of 900 ug/L could be achieved with 0.1 mg/L of phosphorus in solution. Again, at pH 5 the model underpredicts thorium. The major problem with this model is that it does not explain why thorium solubility increases with increasing ionic strength. With phosphate present at pH 3.5, the phosphate species would dominate and thus thorium should become less soluble with increasing ionic strength. Therefore, the phosphate complexation as shown in equation 4.3 does not appear to be a valid model.

4.2.4 Sorption of Thorium on Ferric Hydroxide

The sorption of thorium to clays, oxides and organic matter is well known (Langmuir and Herman, 1980). In general, the sorption increases between pH 2 and pH 6.5. At pH 6.5 sorption is nearly complete. Since thorium is hydrolyzed at pH values greater than pH 3.2, the sorption involves the hydroxo ($ThOH^{3+}$, $Th(OH)_2^{2+}$, $Th(OH)_3^{+}$) complexes. The leachate oxidation tests at pH 3.5 with various initial $FeSO_4$ concentrations enabled the assessment of the importance of thorium adsorption onto precipitated $Fe(OH)_3$. In these experiments, the initial total thorium concentration was at or below the solubility

limit. Thus, thorium removal from the liquid after Fe(II) oxidation is largely due to sorption mechanisms. Using data provided in Table 3-13, the distribution coefficients (K_D) were calculated on the basis of $Fe(OH)_3(s)$ formation. The results are summarized in Table 4-5.

As shown in Table 4-5, the apparent distribution coefficients of the two thorium isotopes are comparable. The reason for the slightly lower K_D value of thorium-230 is not known but may be due to experimental variability rather than significant differences between Th-232 and Th-230 adsorption. In any case, sorption by precipitated ferric hydroxide may have a significant effect on controlling thorium mobility at pH values above 3. The sorption capacity of iron(III) hydroxides may be evaluated from the data at low (1.35 g/L) initial $FeSO_4$. At pH 3.5, the sorption capacity is estimated to be 1.2 mg thorium/g $Fe(OH)_3$ precipitate. At pH values below 3, the sorption of dissolved thorium on solids decreases rapidly with minimal sorption reported at pH values below 2.

4.2.5 Lysimeter Extraction Results

The lysimeter extraction data needs to be interpreted very carefully. The solid liquid ratio in the lysimeter is approximately 1.6:1 versus a typical ratio of 1:4 for the batch agitated studies. Because the pH in the column is variable, the outlet thorium concentrations may well reflect chemical reactions that occur in the column rather than be a direct reflection of the leaching conditions. This is especially true for the weak acid (pH = 3.5 and 5) tests in which substantial pH shifts can occur in the column. These pH shifts may not be greatly noticed in the effluent stream as ferrous iron oxidation in the collection vessel may produce pH conditions much lower than the pH occurring in the columns.

Tailings contain many buffering agents that will include ferric hydroxide, aluminum hydroxide and calcium carbonate. All of these agents are expected to consume some acidity in the pH 2 and 3.5 tests and, as such, thorium levels may not necessarily be reflective of a pH 3.5 condition. Therefore, the effluent thorium levels are well below those anticipated from the batch

TABLE 4-5

DISTRIBUTION COEFFICIENTS (K_D) OF THORIUM ISOTOPES ON $Fe(OH)_3$

Initial $FeSO_4$ Concentration (g/L)	K_D (mL/g) Thorium-232	Thorium-230
1.35	4.02×10^4	2.80×10^4
2.70	1.83×10^4	1.60×10^4
10.90	5.21×10^4	1.45×10^4
21.80	2.08×10^4	1.45×10^4

work. For example, at 0.1 percent calcium carbonate, the lysimeter could consume 14 moles of acidity (as $CaCO_3$). This is equivalent to the acidity contained in 88 bed volumes of leachate water at pH 3.5. At pH 2 on the other hand, only 2 to 3 bed volumes of acid water would be neutralized by $CaCO_3$ dissolution. Therefore, peak concentrations would be expected to occur in the 3 bed volume range. This was the case for the 5 mL/min experiment, but not at 10 mL/min. At 10 ml/min peak levels occurred in the first bed volume which may well be because the calcium carbonate dissolution rate is low.

4.3 GEOCHEMICAL MODEL FOR THORIUM SOLUBILITY

As discussed in Section 4.2.2 and 4.2.3, the sulphate and hydroxo complexes of thorium have a significant effect on thorium solubility at acidic pH values. Is also evident that equilibrium models based on simple complexation reactions are inadequate to describe the total dissolved thorium concentrations at near neutral or alkaline pH conditions. In fact, model predictions were several orders of magnitude below observed concentrations in the leach water. It has been noted (Hertz and Tyree, 1965), that the hydroxo complexes of thorium tend to form large aggregates. These polymeric forms may contain 140 to 150 thorium atoms per solute particle. These aggregates approach colloidal size (450A) in terms of their light scattering properties, but are an order of magnitude smaller than the pore size of a 0.45 filter. From the present experimental database it appears that the concentration of these colloidal thorium hydroxides, or possibly other complexes, is slightly pH dependent. The concentration of these colloidal complexes was found to be proportional to $10^{-0.32pH}$ by the best fit of the residual between experimental data and predictions excluding colloidal complexes. The incorporation of this pH dependent term into the solubility expression for total dissolved thorium yielded the following equation:

$$[Th] = \frac{10^{2.5-4pH}}{f^4} \left((1 + f^{7/4}\, 10^{(pH-3.2)} + f^3\, 10^{(2pH-6.93)} + f^{15/4}\, 10^{(3pH-11.7)} + f^4\, 10^{(4pH-15.9)} + f^4\, 10^{5.45[SO_4^{2-}]} + f^6\, 10^{9.73\,[SO_4^{2-}]^2}\right) + 10^{-(4.17+0.32pH)} \qquad \text{(Eq. 4.3.1)}$$

where:

[Th] = total thorium concentration (moles/L)

f = activity coefficient of divalent cations.

Using Eq. 4.3.1, the predicted total thorium concentration is compared with measured concentrations in Table 4-6.

TABLE 4-6

GEOCHEMICAL MODEL PREDICTIONS FOR THORIUM* (ug/L)

pH	3.5	3.5	3.5	3.5	2	3	4	5	9.6
ionic strength (moles/L)									
f	0.47	0.42	0.32	0.31	0.32	0.32	0.32	0.32	0.47
sulphate (moles/L)	0.025	0.033	0.090	0.164	0.090	0.090	0.090	0.090	0.02
predicted	1740	1960	4480	11,400	3.3×10^{9}**	3.3×10^{5}**	856	393	13.2
measured	1450	2050	6500	11,900	23,800	11,000	910	400	10.3

* $K_{Th} = 2.5$

** at low pH all the thorium hydroxide is leached, therefore themodel results are not applicable.

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As shown in Table 4-6, the agreement between predicted and experimentally observed total thorium concentrations at and above pH 3.5 is excellent. The model describes adequately the effect of sulphate, pH, and the ionic strength on dissolved thorium concentration. It should be noted, however, that the sulphate concentration to be used is the uncomplexed sulphate concentration rather than the total sulphate in solution. At pH 3, the predicted concentration is approximately 30 times higher than the measured value. At this pH,however, significant concentrations of aluminum and ferric hydroxides from the tailings would dissolve. Since both the aluminum ion (Al^{3+}) and the ferric ion (Fe^{3+}) are known to form sulphate complexes, the actual uncomplexed sulphate concentration is likely to be substantially less than indicated. Since the sulphate complexes of thorium are the predominant dissolved species at pH 3, any reduction of the uncomplexed sulphate concentration would have significant effect on the total thorium in solution. At pH 2, virtually all extractable thorium is in solution, hence the predicted solubility in equilibrium with a solid phase is of no significance.

The log K_{Th} value of 2.5 is equivalent to a solubility product K_s^o of $10^{-53.5}$. This value is comparable with a solubility product of $10^{-54.2}$ estimated by Langmuir and Herman (1980) for crystalline thorium oxide (ThO_2).

Although the difference between the two estimate amounts to approximately a 5-fold difference in dissolved thorium concentrations, the solubility product estimated in this study is well within the range reported for thorium oxides.

5.0 CONCLUSIONS

The results of this experimental program indicate that in Elliot Lake tailings approximately 64% of thorium-232 and 80% of the thorium-230 are potentially leachable. These leachable fractions form a nearly ideal solid solution of thorium oxide in which thorium-230 and thorium-228 are trace components by mass. The somewhat higher leachability of thorium-230 gives rise to an enrichment of the thorium-230/thorium-232 activity ratio in the liquid phase.

The expected activity ratio in the liquid phase is 5.61 for an "initial" tailings solid activity ratio of 4.5. As the leaching process progresses, the thorium-230/thorium-232 activity ratio would decline toward 2.5, which is the apparent activity ratio in the un-leachable solid fraction.

A geochemical model has been developed and tested for predicting total dissolved thorium concentrations in leachates. The model takes into account the effect of pH, sulphate, and the ionic strength on dissolved thorium concentrations. Excellent agreements were obtained between observed and predicted total thorium concentrations above pH 3.5. At lower pH values, problems arose when estimating sulphate speciation. At pH 2, dissolution of the solid phase was essentially complete, hence no solubility limit could be reached. The estimated solubility product compared well with published data.

Hydroxy complexes of thorium adsorbed on precipitated iron(III) hydroxides. At pH 3.5, the apparent distribution coefficient (K_D) ranged from 1.5×10^4 to 5×10^4 mL/g. The calculated K_D values for thorium-230 and thorium-232 were comparable. Sorption on precipitating $Fe(OH)_3$ resulted in 95% or higher removal of all dissolved thorium isotopes. The sorption capacity of iron (III) hydroxides was estimated to be 1.2 mg thorium/g $Fe(OH)_3$.

6.0 REFERENCES

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APPENDIX A

ORIGINAL STATEMENT OF WORK

CONTRACT SERIAL NUMBER / NUMÉRO DE SÉRIE DU CONTRAT

CONTINUATION

DSS FILE NUMBER - NUMÉRO DU DOSSIER MAS
15SQ.23317-6-1723

APPENDIX "A"

STATEMENT OF WORK

OBJECTIVES:

To verify and estimate the magnitude of the release of thorium-230 to the environment to improve an understanding of the geochemistry of uranium mill tailings

BACKGROUND:

The National Uranium Tailings Program is striving to develop mathematical models to predict future events pertaining to uranium tailings and to quantify and assign uncertainties to these predictions. To do so, data and information on the pathways of release of contaminants from the tailings in the long term are being obtained. Ra-226 was considered to be the major radioactive contaminant in the tailings and its its physical nature and ensuing reaction pathways have been thoroughly studied. A recent field study at the Lacnor tailings site has however indicated that thorium chemistry is not as well understood as thought and that thorium-230 may also make a significant contribution to the dose to Man.

SCOPE OF WORK:

Proposals are being sought for a combined experimental, theoretical modelling investigation of the geochemistry of thorium in uranium mill tailings for verifying and estimating the magnitude of the release of thorium-230 to the environment. The work involves an experimental study of the release of thorium-230 from a uranium mill tailings sample as a function of pH and Fe(II) concentration of the eluant and of the co-precipitation of thorium-230 as a function of the pH and Fe(III) concentration in sulphate medium. The experimental results will be compared with theoretical values calculated from an appropriate equilibrium model to assess the suitability of the model in describing thorium geochemistry.

PROPOSED WORK PLAN

(1) Characterization of Uranium Mill Tailings Sample

The contractor will procure a sufficient quantity of unoxidized, "fresh" uranium mill tailings to perform the work described below.

The collected sample will be analyzed in duplicate for total iron, calcium, sulphate, total thorium, thorium-230
Two separate samples of porewater will be

collected, its pH measured and analyzed for total iron, calcium, sulphate, total thorium and thorium-230.

Two test portions will be thoroughly washed with distilled water and filtered. Both the solids and the washings will be analyzed for total thorium and thorium-230. The solids will also be analyzed for the iron, thorium and thorium-230 present as the hydrous oxide/hydroxide by the leaching method using sodium dithionate, sodium citrate and citric acid described by Anderson and Jenne in Soil Science 109, 163-169(1970).

(2)Thorium geochemistry

The following tests will be performed at a scale large enough to provide sufficient leachate(1-2 L) for chemical and radionuclide analysis.

Test portions of the uranium mill tailings will be batch leached under an inert atmosphere with ferrous sulphate solution(13.5 g/L $FeSO_4$) at pH 5.4,3.2. The reaction time needed to attain equilibrium must be determined experimentally.

Test portions of the uranium mill tailings will be batch leached under an inert atmosphere with ferrous sulphate solutions at 21.8 g/L, 10.9 g/L, 2.71 g/L and 1.35 g/L at pH 3.5. The reaction time needed to attain equilibrium must be determined experimentally.

For all experiments, the leachates will be analyzed for total Fe, calcium, sulphate, total thorium and thorium-230. The pH of the leachate will also be measured.

The pH of each leachate is adjusted to 4; the Fe(II) is oxidized to Fe(III) with H_2O_2 and the solution is allowed to stand for approximately 2 weeks. The sample is filtered and the filtrate and precipitate are analyzed for total iron, calcium, sulphate, total thorium and thorium-230.

(3) Kinetics of thorium geochemistry

Four test portions of uranium mill tailings samples will be placed in lysimeters. These will be leached with one of the $FeSO_4$ solution(13.5g/L) at the pH, and the $FeSO_4$ solution(21.8 - 1.35g/L) at pH 3.5 showing maximum and minimum thorium leaching in (2). The eluant will be analyzed for total thorium and thorium-230 after one or more bed volumes have been collected, depending on the rate of thorium-230 release. The pH of the eluant will also be measured. Three leaching rates(ratio 1:5:10) will be used with the lowest being agreed to by the contractor and the scientific authority.

(4) Modelling of thorium geochemistry

Using an appropriate equilibrium model, theoretical thorium geochemical behaviour based on the analytical information found in (2) is compared to the experimental thorium values to assess the suitability of the model to uranium mill tailings and, where necessary, implement changes to the model to attain consistency with observed thorium geochemical behaviour.

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CONTRACT SERIAL NUMBER / NUMÉRO DE SÉRIE DU CONTRAT

CONTINUATION

DOS FILE NUMBER - NUMÉRO DU DOSSIER MAS
15SQ.23317-6-1723

DELIVERY SCHEDULE/DELIVERABLES

Monthly progress reports in letter format are to be submitted in two copies to the Scientific Authority. These reports must summarize:

- work done in the previous period
- significant achievements
- potential problem areas
- the work planned for the next period

Regular reference should be made to the Statement of Work, the project schedule and the cost estimate in the proposal.

A draft final report is to be submitted in three copies to the Scientific Authority on or before August 1, 1986. The Scientific Authority will return one copy with his comments and suggestions to the contractor within two weeks after receiving the draft final report.

Twenty-five copies of the final report are to be submitted to the Scientific Authority on or before August 31, 1986. The final report must also contain an executive summary.

APPENDIX B

INTERPOLATION OF LYSIMETER TEST RESULTS

APPENDIX B
INTERPOLATION OF LYSIMETER TEST RESULTS

In the execution of the lysimeter tests only 4 bed volumes of leachate out of a total of 10 bed volumes were submitted for thorium and thorium-230 analysis. In order to obtain an estimate of the analysis of the other bed volumes the four thorium and thorium-230 concentrations obtained for the first, third, sixth and tenth bed volumes were plotted against bed volume flow through the column. By interpolation of these results estimates of thorium and thorium-230 concentrations were obtained for the second, fourth, fifth, seventh, eighth and ninth bed volume.

It was then possible to arrive at an estimate of the total thorium and thorium-230 leached from the tailings in each lysimeter test by totalling the contents of each bed volume to give the total content of thorium and thorium-230 in the 10 L of leachate passed through the column for each test.

The preparation and analysis of the tailings residue in the column at the end of the column leach was not part of the test program. Hence the total thorium and thorium-230 present in the column leachate was compared against the content in the tailings solids feed to the column to obtain an estimate of the thorium and thorium-230 extracted for each lysimeter test. The tailings solids head assay used for these calculations was the analytical head of 0.01525% Th and 2.5 Bq/g Th-230. The amount of tailings to each column was 1,395 g hence the estimated content of thorium in the tailings to each column was 3,487.5 Bq of Th-230 and 212.738 mg of Th.

The extraction calculations for each lysimeter test are summarized in Tables B-1 to B-12. Detailed graphs were used for interpolating the thorium and thorium-230 analyses listed in these tables. The general format of the graphs are presented in Figures B-1 to B-8. The extraction results have been summarized in the main text of the report in Table 3-18 of Section 3.7.2.

TABLE B-1

TEST CONDITIONS - pH 2, 13.5 g/L $FeSO_4$, 20 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	6.5	250
2	5.5	205
3	4.5	170
4	2.9	102
5	1.4	42
6	0.5	4
7	0.5	4.5
8	0.6	5
9	0.7	5.5
10	0.8	6
Total in leachate	23.9 Bq	794 µg

Percent Extraction:

Th-230 $\frac{23.9}{3,487.5} \times 100 = 0.7\%$

Th $\frac{794}{212,738} \times 100 = 0.4\%$

TABLE B-2

TEST CONDITIONS - pH 2, 13.5 g/L $FeSO_4$, 10 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	220	23,800
2	212	18,000
3	200	12,500
4	165	10,300
5	137	8,800
6	120	7,650
7	111	7,100
8	103	6,600
9	96	6,100
10	90	5,760
Total in leachate	1454 Bq	106,610 µg

Percent Extraction: Th-230 $\frac{1,454}{3,487.5} \times 100 = 41.7\%$

Th $\frac{106,610}{212,738} \times 100 = 50.1\%$

TABLE B-3

TEST CONDITIONS - pH 2, 13.5 g/L $FeSO_4$, 5 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	140	6,400
2	290	16,500
3	470	27,700
4	340	20,800
5	240	14,700
6	160	10,300
7	120	7,500
8	90	5,300
9	64	3,500
10	40	2,170
Total in Leachate	1954 Bq	114,870 µg

Percent Extraction: Th-230 $\frac{1,954}{3,487.5} \times 100 = 56.0\%$

Th $\frac{114,870}{212,738} \times 100 = 54.0\%$

TABLE B-4

TEST CONDITIONS - pH 5, 13.5 g/L $FeSO_4$, 20 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	0.9	50
2	0.86	30
3	0.8	13
4	0.68	14
5	0.49	15
6	0.35	16
7	0.39	15
8	0.44	14
9	0.49	12
10	0.55	10
Total in Leachate	5.95 Bq	189 µg

Percent Extraction: Th-230 $\frac{5.95}{3,487.5} \times 100 = 0.17\%$

Th $\frac{189}{212,738} \times 100 = 0.09\%$

TABLE B-5

TEST CONDITIONS - pH 5, 13.5 g/L $FeSO_4$, 10 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	0.7	45
2	0.82	40
3	0.9	35
4	0.79	28.5
5	0.66	21
6	0.55	15
7	0.59	21
8	0.66	27.5
9	0.73	34
10	0.8	40
Total in Leachate	7.2 Bq	307 µg

Percent Extraction: Th-230 $\frac{7.2}{3,487.5} \times 100 = 0.21\%$

Th $\frac{307}{212,738} \times 100 = 0.14\%$

TABLE B-6

TEST CONDITIONS - pH 5, 13.5 g/L $FeSO_4$, 5 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	3.0	19
2	1.46	12.3
3	0.7	8.5
4	0.5	7.8
5	0.4	7.4
6	0.35	7.0
7	0.36	6.8
8	0.39	6.6
9	0.41	6.5
10	0.45	6.5
Total in Leachate	8.02 Bq	88.4 µg

Percent Extraction: Th-230 $\frac{8.02}{3,487.5} \times 100 = 0.23\%$

Th $\frac{88.4}{212,738} \times 100 = 0.04\%$

TABLE B-7

TEST CONDITIONS - pH 3.5, 21.8 g/L $FeSO_4$, 20 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	0.6	25
2	0.9	40
3	1.2	60
4	2.6	170
5	5.7	325
6	7.5	460
7	7.7	475
8	7.8	490
9	7.9	505
10	8.0	520
Total in Leachate	49.9 Bq	3,070 µg

Percent Extraction: Th-230 $\frac{49.9}{3,487.5} \times 100 = 1.4\%$

Th $\frac{3,070}{212,738} \times 100 = 1.4\%$

TABLE B-8

TEST CONDITIONS - pH 3.5, 21.8 g/L $FeSO_4$, 10 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	1.1	45
2	1.1	45
3	1.1	45
4	2.0	120
5	3.6	230
6	5.5	340
7	10.5	700
8	17.6	1,230
9	28	1,940
10	45	3,040
Total in Leachate	115.5 Bq	7,735 µg

Percent Extraction: Th-230 $\frac{115.5}{3,487.5} \times 100 = 3.3\%$

Th $\frac{7,735}{212,738} \times 100 = 3.6\%$

TABLE B-9

TEST CONDITIONS - pH 3.5, 21.8 g/L $FeSO_4$, 5 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	1.2	18
2	0.9	17
3	0.7	16
4	3.5	250
5	9.6	670
6	16	1,180
7	24.6	1,860
8	32.6	2,320
9	41	2,860
10	50	3,420
Total in Leachate	180.1 Bq	12,611 µg

Percent Extraction: Th-230 $\frac{180.1}{3,487.5} \times 100 = 5.2\%$

Th $\frac{12,611}{212,738} \times 100 = 5.9\%$

TABLE B-10

TEST CONDITIONS - pH 3.5, 1.35 g/L $FeSO_4$, 20 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	0.25	10.0
2	0.16	4.8
3	0.11	3.5
4	0.16	3.1
5	0.25	2.8
6	0.35	2.5
7	0.44	2.1
8	0.51	1.6
9	0.58	1.0
10	0.65	0.50
Total in Leachate	3.46 Bq	31.9 µg

Percent Extraction: Th-230 $\frac{3.46}{3,487.5} \times 100 = 0.10\%$

Th $\frac{31.9}{212,738} \times 100 = 0.02\%$

TABLE B-11

TEST CONDITIONS - pH 3.5, 1.35 g/L $FeSO_4$, 10 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	0.11	1.9
2	0.11	1.4
3	0.13	1.0
4	0.4	1.5
5	0.88	2.2
6	1.5	3.0
7	0.86	2.45
8	0.5	1.85
9	0.28	1.45
10	0.11	1.1
Total in Leachate	4.88 Bq	17.85 µg

Percent Extraction: Th-230 $\frac{4.88}{3,487.5} \times 100 = 0.14\%$

Th $\frac{17.85}{212,738} \times 100 = 0.01\%$

TABLE B-12

TEST CONDITIONS - pH 3.5, 1.35 g/L $FeSO_4$, 5 mL/min

Bed Volume (L)	Th-230 (Bq/L)	Th (µg/L)
1	0.35	11
2	0.48	7.7
3	0.60	4.5
4	0.45	2.2
5	0.32	1.5
6	0.25	1.2
7	0.21	1.15
8	0.19	1.1
9	0.17	1.05
10	0.16	1.0
Total in Leachate	3.18 Bq	32.4 µg

Percent Extraction: Th-230 $\frac{3.18}{3,487.5} \times 100 = 0.09\%$

Th $\frac{32.4}{212,738} \times 100 = 0.02\%$

FIGURE B-1
Th-230:pH 2,13.5 g/L FeSO4

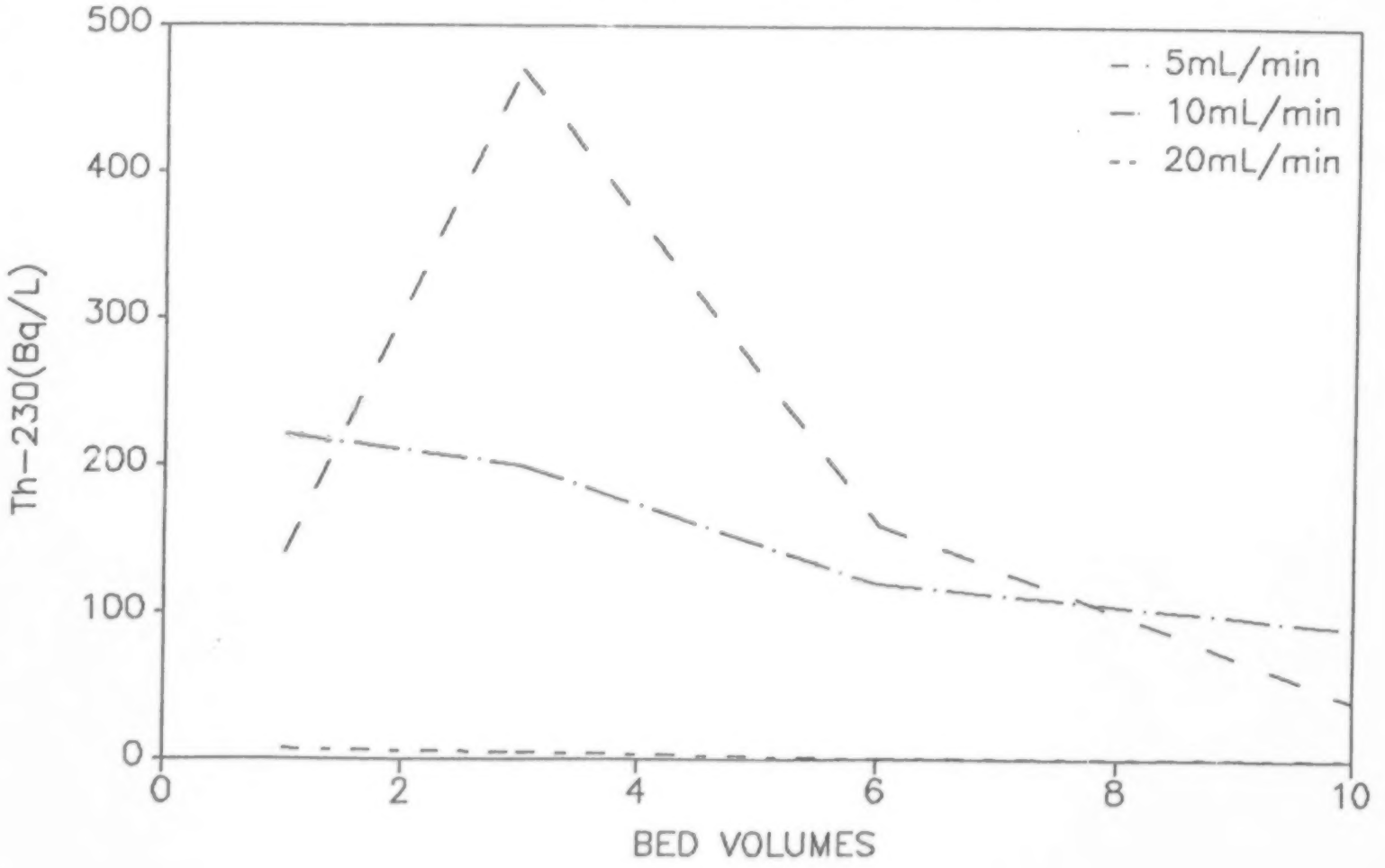

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FIGURE B-2
Th:pH 2,13.5 g/L FeSO4

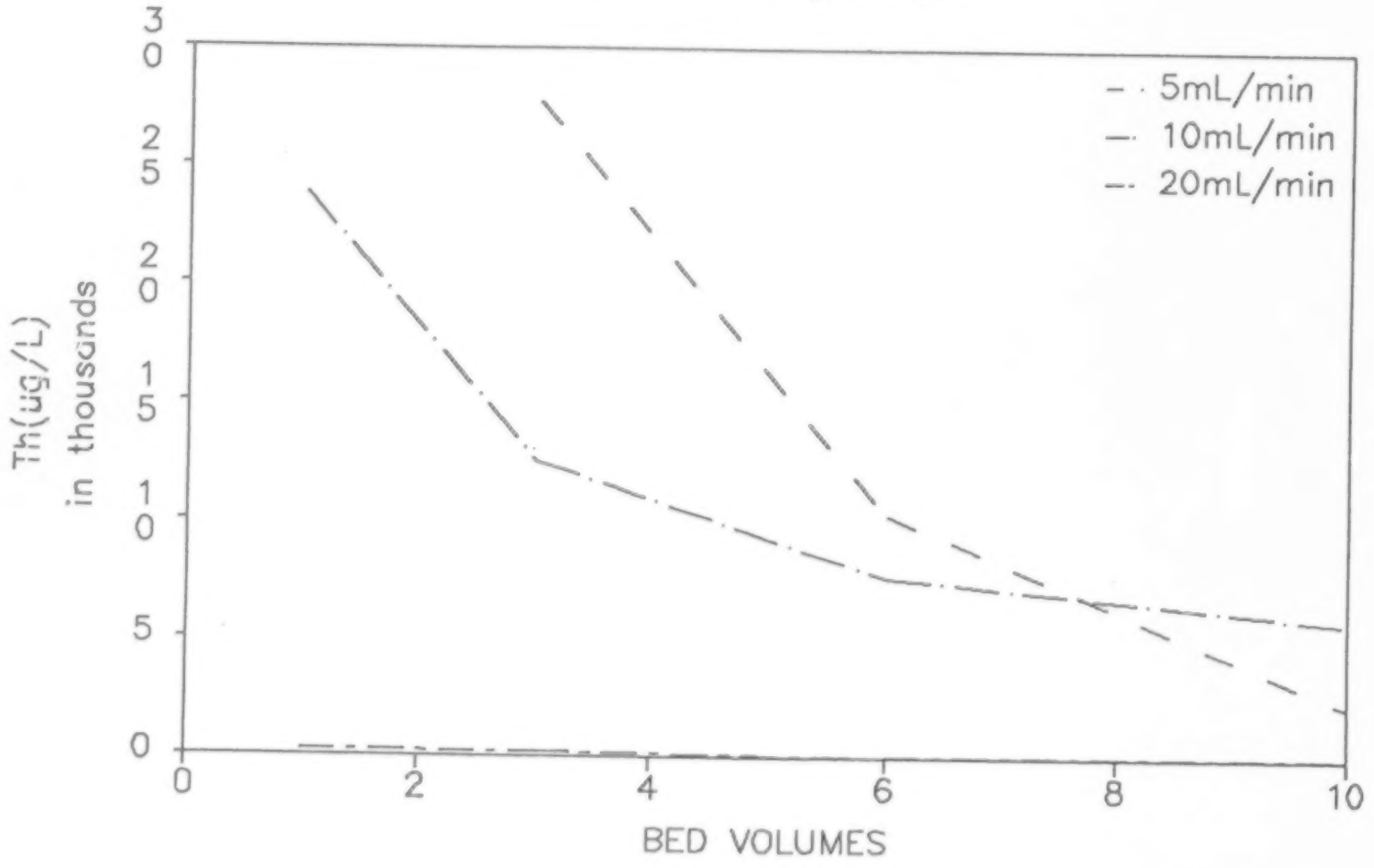

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FIGURE B-3
Th-230:pH 5,13.5 g/L FeSO4

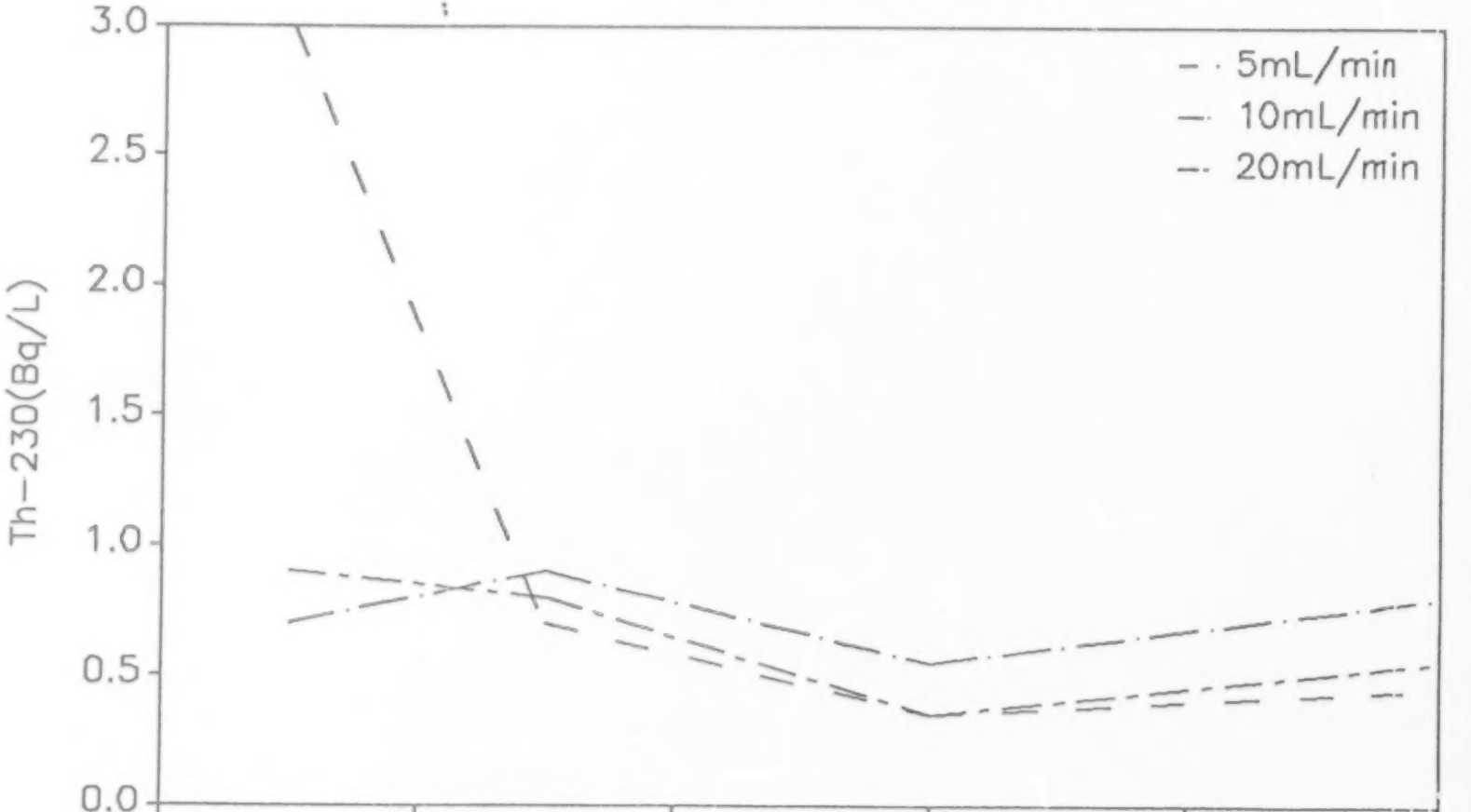

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FIGURE B-4
Th:pH 5,13.5 g/L FeSO4

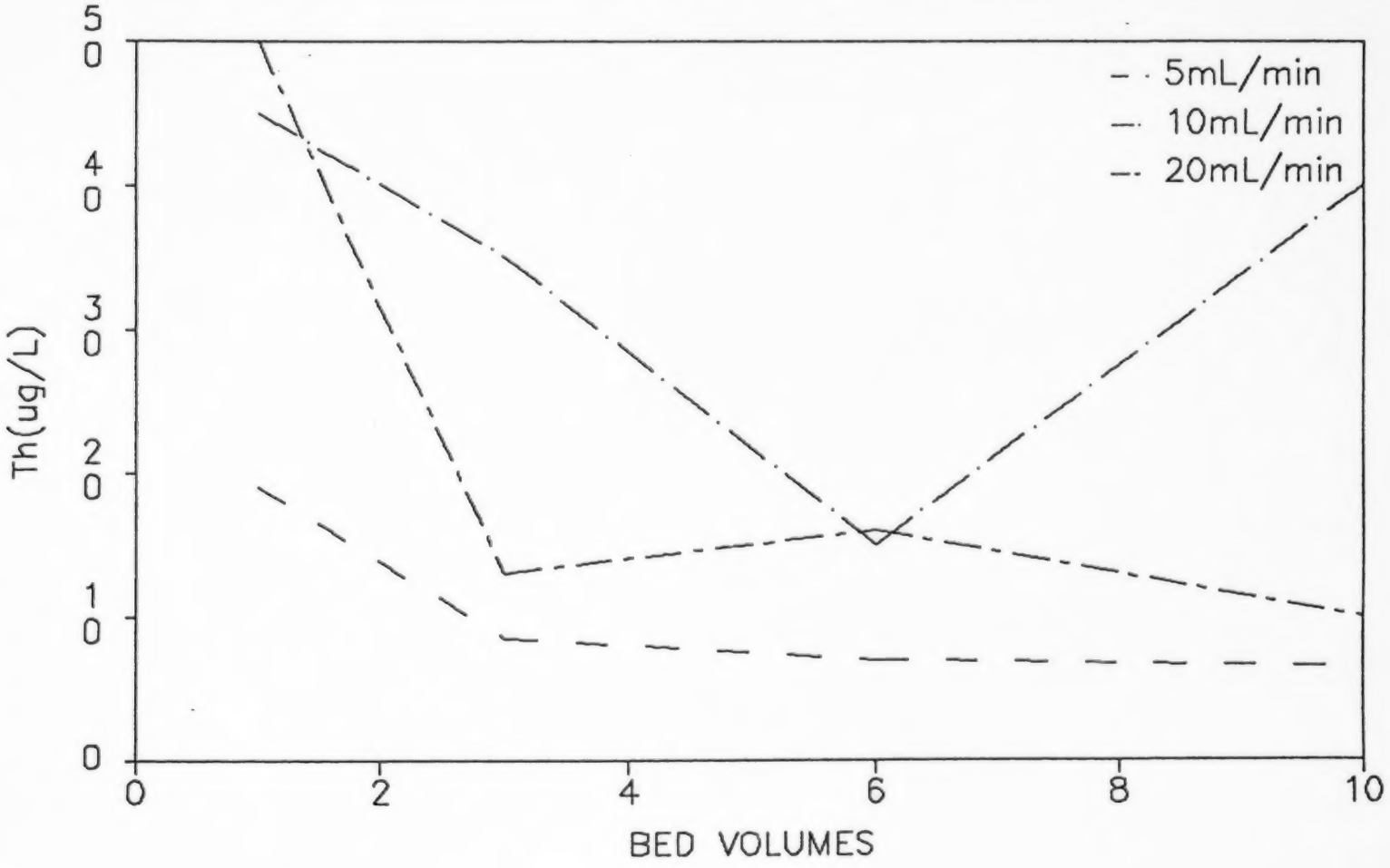

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FIGURE B-5
Th-230:pH 3.5,21.8 g/L FeSO4

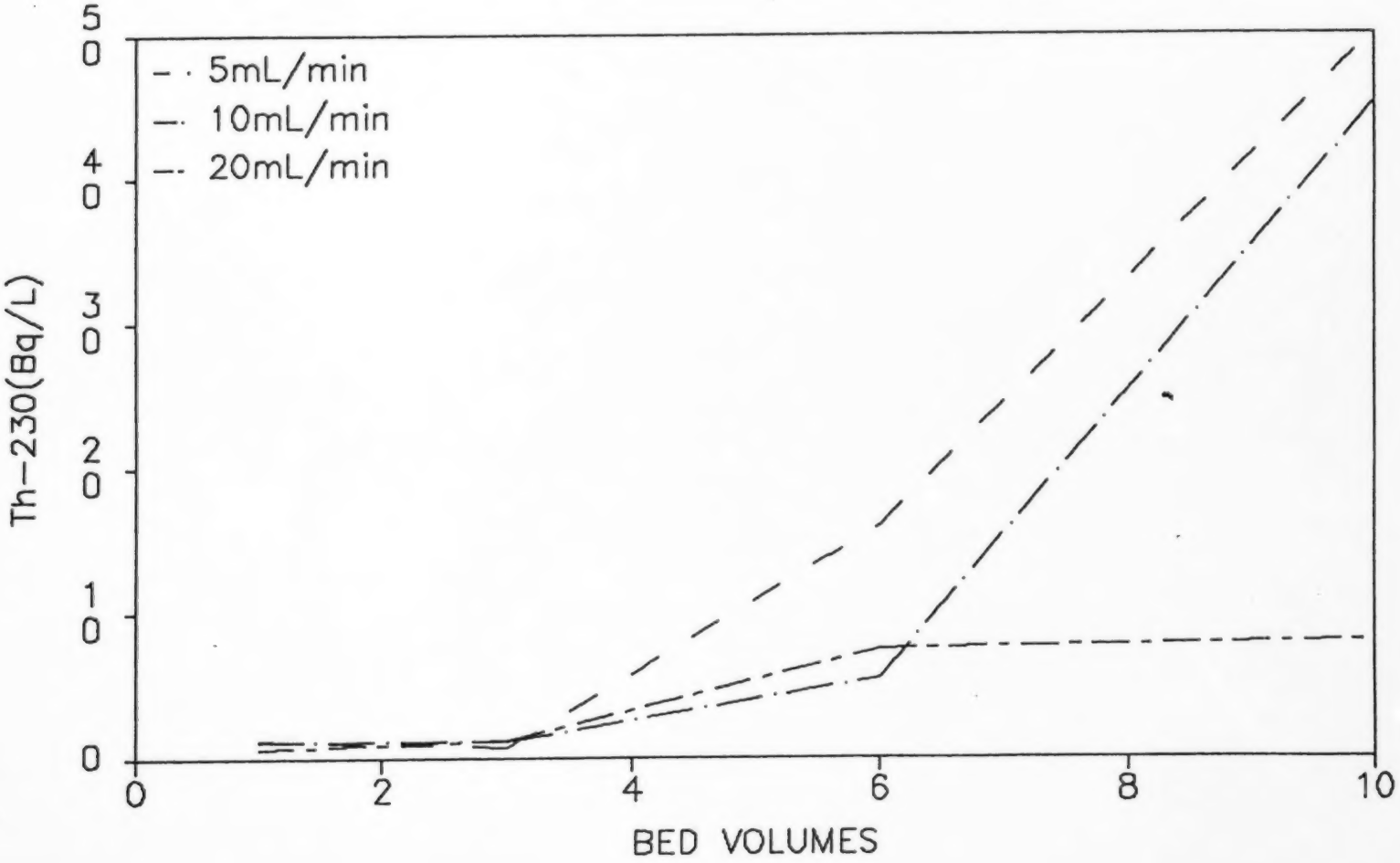

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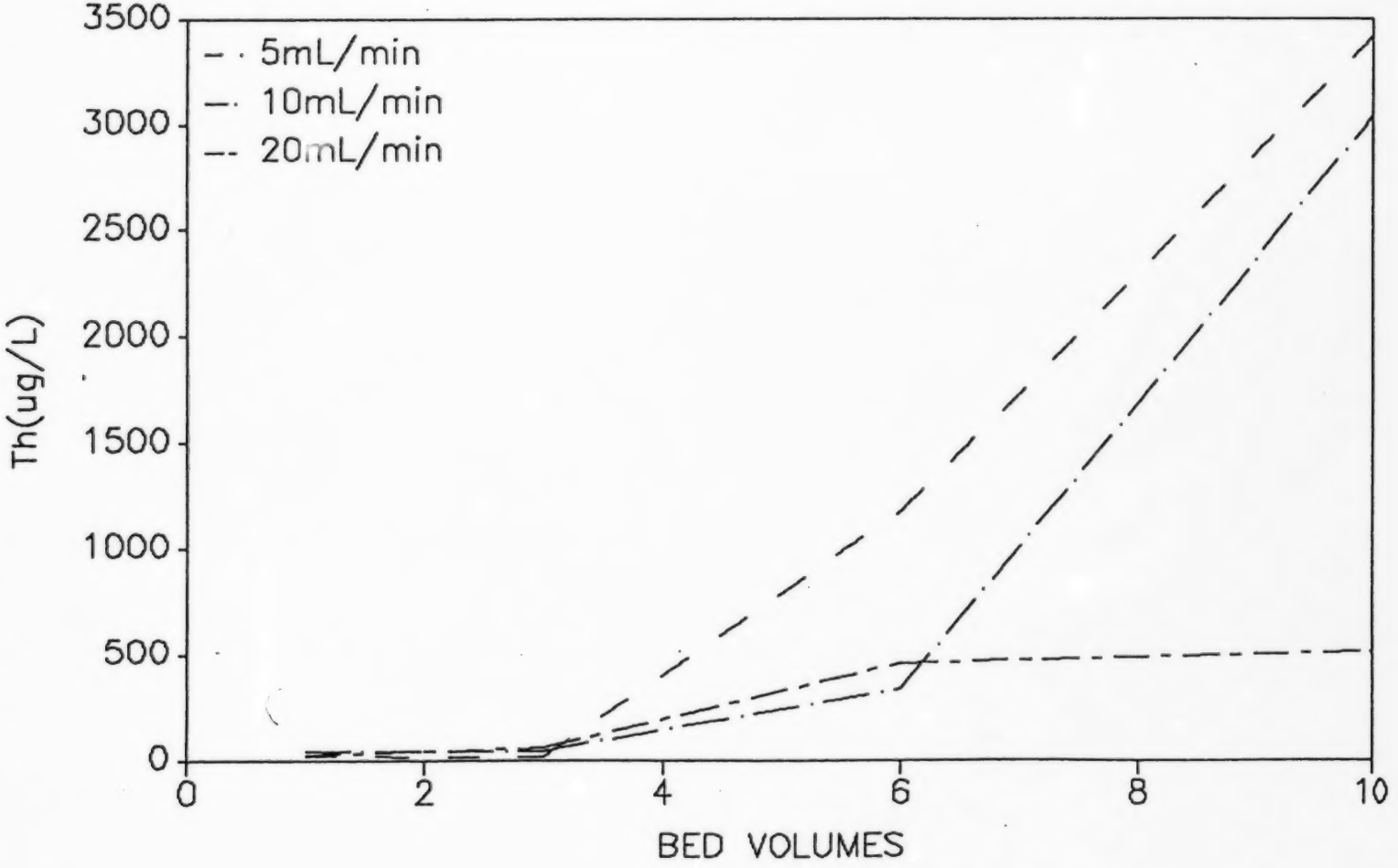
FIGURE B-6
Th:pH 3.5,21.8 g/L FeSO4



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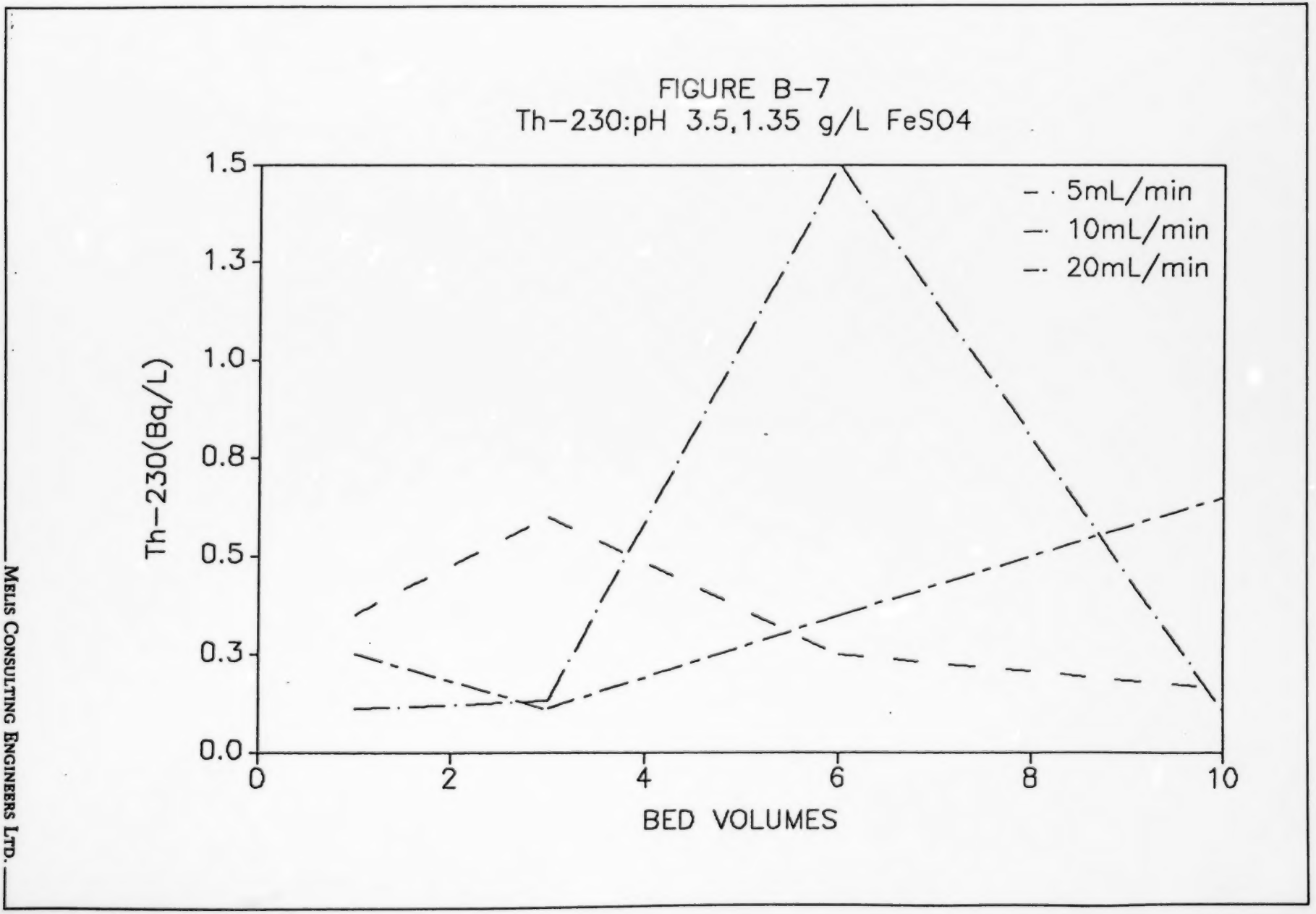

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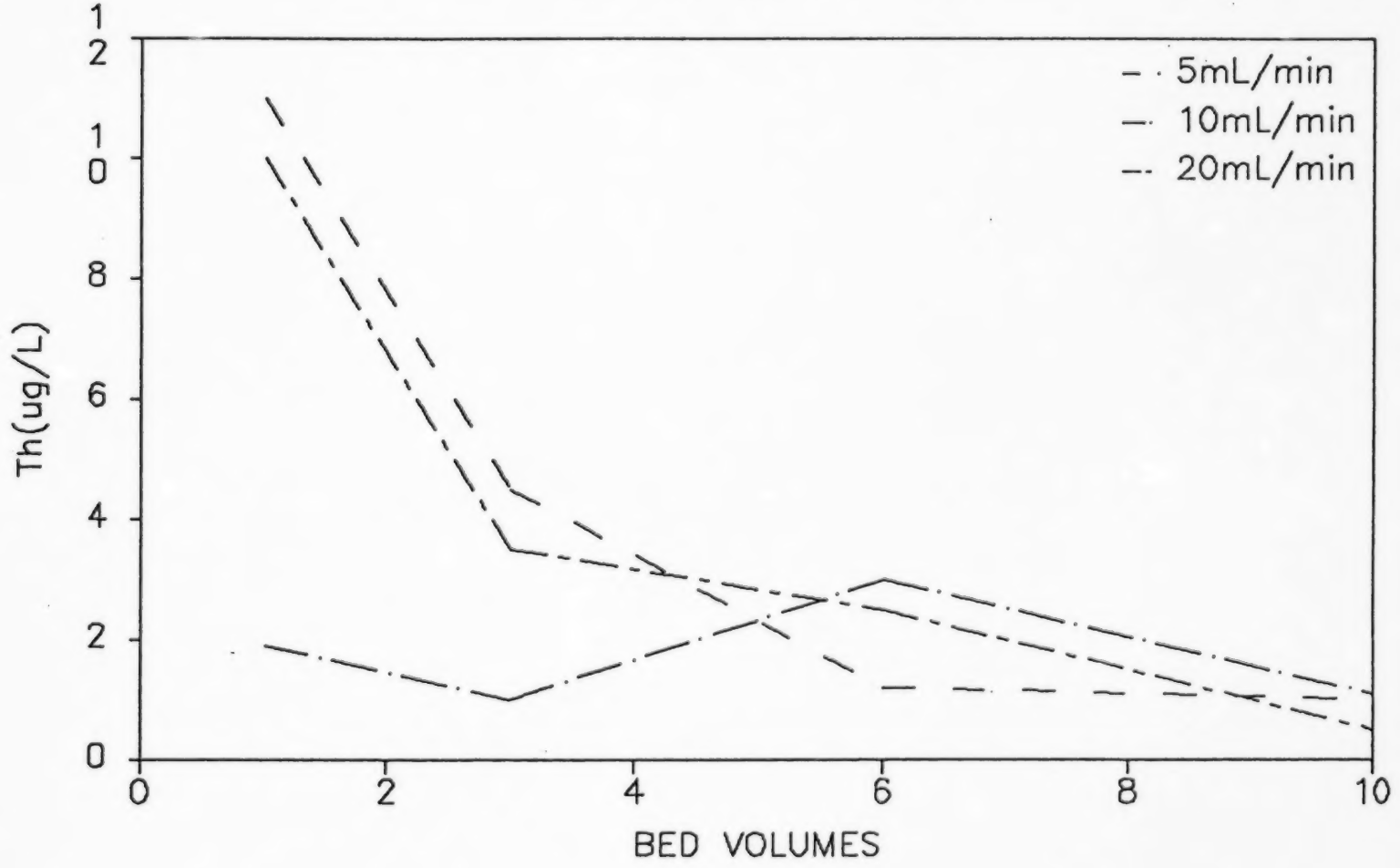
FIGURE B-8
Th:pH 3.5,1.35 g/L FeSO4



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APPENDIX C

THORIUM-230 AND THORIUM-232 ANALYTICAL METHODS

SASKATCHEWAN RESEARCH COUNCIL ANALYTICAL SERVICES

Thorium-230

Tracer: Thorium-234

Sample decomposition: Potassium pyrosulphate fusion

Thorium is separated from prepared sample solutions by coprecipitation with barium sulphate. Barium sulphate is dissolved in a strongly alkaline solution of ethylenediaminetetraacidic acid. Thorium is precipitated as hydroxide with 50 µm cerium carrier. The precipitate is mounted on a 25 mm 0.2 micron membrane filter for alpha spectrometry. Alpha spectrometry is performed using a vacuum chamber mounted surface barrier detector.

Reference Standard:

Std#1 Amersham aged thorium nitrate

Std#2 Alfa Chemicals thorium oxide 99.9%

It was assumed that Th-230 would give the same response as Th-232 and Th-228 from these standards (i.e. cpm/pCi).

Detection Limit = 0.01 Bq/g

Precision = 0.18 - 0.37 Bq ± 10%

>0.37 Bq ± 5%

SASKATCHEWAN RESEARCH COUNCIL ANALYTICAL SERVICES

Thorium-232 by Plasma-Mass Spectrometry

Liquid samples were analyzed for Th-232 by monitoring the 232 mass channel while the solution was aspirated into a V.G. Plasmaquad instrument. Calibrations were performed before and after every three samples. Some samples required a 10-fold dilution to reduce the dissolved solids to below 2000 mg/L. Less concentrated samples were analyzed directly. The technique has a detection limit of 0.2 µg/L for the solution aspirated. For samples with a 10-fold dilution, the detection limit would be 2 µg/L. The precision above 10 µg/L is approximately ±5% (1 sigma). Spikes of several samples were prepared and all results were within ±10% of the expected value.